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ELECTROLYTIC CORROSION OF IRON BY DIRECT CURRENT.

BY

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IN electric railways the rails are practically always used as return conductors. Since they are grounded, a part of the return current leaves the rails and passes through the ground, and if the voltage drop in the rails is considerable this stray current through the ground may be considerable and cause more or less serious corrosion of rails, gas and water pipes, iron structures and other metal parts located in the ground. The problem of studying the corrosion produced by stray direct currents in the ground, so as to reduce the damage caused by them to a minimum, thus is of great importance.

This problem is frequently attacked by measuring the potential difference between the different points of the rail return system and other metal parts in the ground, estimate therefrom the stray current, and from this judge on the amount of electrolytic corrosion which may be expected by Faraday's law. There is, however, some doubt, from the experience of electric railways, whether the passage of a stray current between metal parts in the ground necessarily involves corrosion in accordance with Faraday's law, or whether it may not be possible that currents

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pass from metal to ground without corresponding corrosion of the metal.

As iron is the metal which is most frequently exposed and therefore of greatest importance, an investigation was started on the corrosion of iron under the influence of an electric current in Dr. Steinmetz's laboratory, and some preliminary results are given in the following:

The first electrolyte experimented with was a 1 per cent. solution of ammonium nitrate, as nitrates and ammonia salts are the most probable conducting compounds in soils, especially in cities.

Sheet iron plates of 0.6 mm. thickness were used, carefully cleaned by hydrochloric and nitric acid and then mechanically. They were immersed in quart jars, each containing approximately 800 cc. of electrolyte.

The plates dipped 9 cm. into the electrolyte.

As negative were chosen plates of 14 cm. length, 5 cm. width, giving 90 cm.^{2} submerged surface.

As positive were chosen plates of 14 cm. length and of different widths, from 0.6 cm. to 10 cm.

The current was maintained constant, from a storage battery, at .040 ampere, corresponding to current densities from 36 amperes to 2.2 amperes per m^2.

After the test the plates were carefully cleaned with distilled water and chalk, and then weighed again.

In calculating the theoretical corrosion, the value of .29 mg. of iron per coulomb was used.

The duration of this test was 98 hours.

The corrosion in no case approached the theoretical value, but varied from one-tenth to one-third of the theoretical value, as follows:

In general, it was lower at higher current densities.

Herefrom it seems to follow that it is not feasible to estimate the electrolytic corrosion of iron structures in the ground from the amount of stray current passing from these structures.

Current density, amperes per m^2	36	18	9	4.5	2.25
Corrosion, per cent. of theoretical ..	10.5	18.0	17.1	35.1	34.2

As the electrolytic corrosion of the iron was found much lower than the theoretical value, tests were made to see whether this is due to a partial corrosion, or due to periods in which no

corrosion takes place, that is, the iron is "passive," and to find the conditions under which the iron is passive, that is, does not corrode as positive terminal.

For this purpose, 10 cells were made up, 800 cm.^{3} electrolyte, 1 per cent. solution of ammonium nitrate, with iron plates of 14 cm. x 1.25 cm., dipping 9 cm. into the electrolyte, and operated in series, with 50 milliamperes of current, corresponding to a current density of about 22 amperes per m^2.

In two cells the plates were taken out, cleaned and weighed very frequently, in two cells less frequently, and in two cells left in continuously. In two cells the plates were put in the electrolyte one hour before the current was put on; two cells were left without current and used to observe the spontaneous or chemical corrosion of the plates by the electrolyte.

In half the cells the electrolyte was changed after the cell had been running 24 hours; in the others the electrolyte was not changed.

The results of this and the following test are given in Table I, and some are plotted in Figure 1.

It seems that there is no partial corrosion, but the iron is either *passive*, that is, practically no corrosion at all takes place, or the iron is *active*, that is, the full theoretical corrosion occurs. Fractional values of the theoretical corrosion are observed only where the cell has been operated continuously for a considerable time, and apparently had started active and then become passive.

The average corrosion during the active periods is 49.6 mg. per hour, or, if counting only the shorter periods—during which a change of state is less probable—55.1 mg. per hour, while the theoretical attack is 52.2 mg. per hour, and is shown by the dotted lines in Figure 1.

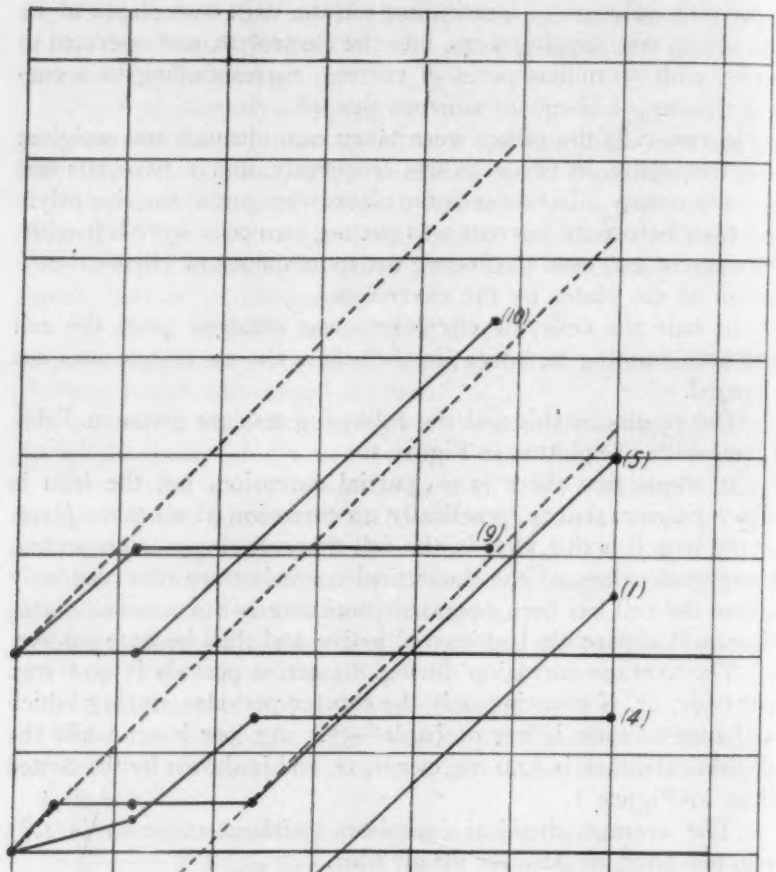
The average chemical corrosion (without current) is 1.85 mg. per hour, or 0.82 per m^2 an hour.

The corrosion of the anode during the active period thus is somewhat greater than the theoretical, as expected from chemical corrosion.

The average corrosion of the anode during the passive period is .20 mg. per hour, that is, less than ½ per cent. of the theoretical, and is only about 11 per cent. of the chemical corrosion. That is, the passage of a current from a *passive anode* protects the same from spontaneous or chemical corrosion.

The average corrosion of the cathode was .40 mg. per hour with a *passive* anode, and .23 mg. per hour with an *active* anode.

FIG. 1.



Electrolytic corrosion of iron by direct current. 1 % ammon. nitrate solution, 22 amp. p. m².

That is, if the anode is passive and does not corrode, the cathode corrodes about twice as much as if the anode is active and cor-

rodes. Even in this case, however, the corrosion of the cathode is only about 20 per cent. of the chemical corrosion, and about twice as much as that of the anode.

It thus follows that during the passive state the corrosion of two iron plates is by the passage of the current reduced to a small fraction of the chemical corrosion. That is, under certain conditions (passive state), the passage of a direct current protects both of the iron terminals between which it passes.

The active state occurred eight times.

The passive state occurred ten times.

Three times the corrosion was intermediate between that of the active and the passive state. Of these, two were long continuous runs, in which the behavior of the cells made a spontaneous change from the active to the passive state probable.

Handling the plates, that is, taking them out, cleaning and weighing, frequently changes the state:

6 times from active to passive,
4 times from passive to active,
3 times the plate remained passive,
Possibly 1 time the plate remained active.

Change of electrolyte changed

1 time from passive to active,
1 time left the plates passive,
1 time probably left the plates active,
1 time probably changed from passive to active.

No definite effect of a change of the electrolyte on the state of the plates is thus shown. As at the end of the run the electrolyte still gave the ammonia reaction and the nitric acid reaction, this is reasonable.

The voltage per cell was either low, about 1 volt, or high, 2.7 volts, but intermediary voltages were observed only in two cases, at the end of a long active run, probably as the result of an increase of the resistance of the electrolyte.

The active state of corrosion was always accompanied by low voltage; the passive state, of no corrosion, by high voltage; and the voltage of the cell was found a good indicator of its state, and where a cell changed from active to passive state this was shown by the rise of voltage.

The electrolyte and the deposit formed in the cell seem to give an indication of the state of the anode:

In all cells in which the anodes were passive at least during most of the time, and more particularly the latter part of the run, the electrolyte was clear, or only slightly yellow, and only little deposit was formed, of a yellow-brown color, apparently ferric hydrate.

In all cells in which the anodes were active and greatly corroded the electrolyte was very dirty, and masses of deposit formed. This deposit was of a dirty greenish-black color, indicating apparently ferrous hydrate.

Interesting was one cell in which active corrosion had taken place, but towards the end of the run the voltage had become high and the anode apparently passive. This cell also had a dirty electrolyte and a very large amount of deposit, but the deposit had turned brownish-black towards the end of the run, consisting apparently largely of ferric hydrate. It seems that during the passive period the deposit of ferrous hydrate, formed during the preceding active period, had been oxidized to ferric hydrate.

It thus seems that the active state is accompanied by the formation of the lower hydrates of iron, of greenish-black color, while during the passive state only the higher ferric hydrate can exist.

To investigate how the passive and active state of the iron depend on the method of starting the current, and more particularly whether starting under high current produces passivity, and immersion in the electrolyte without current activity, four cells were started at high current density, and the current then reduced. The series resistance was greatly reduced, the plates then put into the cell without electrolyte, and the electrolyte poured in while the voltage was on, so that the current started simultaneously with the immersion of the electrolyte, at about 430 amperes per m^2. The current was immediately reduced to the normal value of .05 ampere, or 22 amperes per m^2.

All three cells were immediately passive, gave high voltage, and gas on the positive electrode. The positive plate remained bright, the negative turned yellow by a thin yellow deposit of ferric hydrate.

After three hours' running, one cell was short-circuited for

one hour and the electrolysis then continued for 14½ hours more. After the short circuit, the voltage was low, the cell active, and after weighing the plate the corrosion was found, the theoretical amount corresponding to the active period.

A second cell was started once more, in the same manner, and again found passive, with no appreciable corrosion, and high voltage.

Then two cells were made up, by heating the passive plates in the Bunsen flame to incandescence, until covered with a thin layer of scale (18 and 27 mg.), and one cell started immediately, the other after immersion in the electrolyte for one hour, but in both cases the start was made at excess current and the current immediately reduced. Both cells gave high voltage, 2.7, and showed no corrosion, during a long run (118 hours).

After 44½ hours' run one of the cells was once more short-circuited for two hours and the run then continued. The cell remained passive, the voltage high, and practically no corrosion.

Herefrom it seems:

(1.) Starting with the power on, so that the current starts simultaneously with the immersion of the iron into the electrolyte, causes the passive state of no corrosion, at least if the current density in the moment of start is high.

(2.) Submersion of the plate in the electrolyte for some time before the start, or remaining in the electrolyte without the current on for some time during the run, tends to produce the active state.

(3.) The presence of scale on the plates does not seem to have any effect in producing the active state.

(4.) During the passive state only ferric hydrate appears in the cells, on negative plate and in the electrolyte, while the active state always seems to be coincident with the formation of ferrous compounds, though, if followed by the passive state, these ferrous compounds are converted into ferric hydrate.

Thus far only 1 per cent. solution of ammonium nitrate, cp. cryst., had been used as electrolyte.

To investigate other electrolytes, 18 cells were made up, of standard size plates: 14 x 1.25 cm. 1 per cent. solutions of various electrolytes were used, all cp. cryst., and of each electrolyte two cells were made up, one being connected into the circuit on 0.02 ampere (9 amperes per m^2), the other left as check of the chemical corrosion.

The order of electrolytic corrosion, in per cent. of the theoretical value, during a run of 70 hours, was found:

TABLE I.

		Mg. per hour	Avg. volts
Potassium bichromate	.34%	= .07	4.1
Potassium carbonate	2.75	= .58	3.7
Potassium nitrate	25.0	= 5.25	2.5/3.5
Ammonium nitrate	37.8	= 7.93	.8/2.4
Ammonium carbonate	38.2	= 8.0	2.5/3.7
Potassium chloride	102.2	= 21.5	1.9
Ammonium chloride	102.3	= 21.5	1.3
Ammonium sulfate	102.7	= 21.6	3.7
Potassium sulfate	102.8	= 21.6	1.9

The order of chemical corrosion in the check cells is, in mg. per hour:

TABLE II.

	Mg. per hour	Mg. per m² per hour
Potassium bichromate	.01	= 0.004
Potassium nitrate	.34	= 0.15
Potassium carbonate	.36	= 0.16
Potassium chloride	.55	= 0.245
Potassium sulfate	.59	= 0.26
Ammonium carbonate	.61	= 0.27
Ammonium sulfate	.64	= 0 285
Ammonium chloride	.91	= 0.405
Ammonium nitrate	1.75	= 0.78

Potassium carbonate, nitrate and bichromate give gas at both plates.

Potassium chloride and sulfate, and ammonium sulfate and carbonate give gas at the negative, but not at the positive plate. In ammonium chloride and nitrate the electrolyte became so muddy that the plates could not be seen.

In potassium bichromate and carbonate the electrolyte remained clear and colorless; in potassium nitrate, chloride and sulfate it remained fairly clear, but slightly yellow; in ammonium sulfate, nitrate and carbonate slightly muddy and slightly yellow; in ammonium chloride the electrolyte became opaque greenish-black.

The deposit was large and greenish-black in potassium and ammonium sulfate and chloride, showing ferrous hydrate. In these the corrosion was the theoretical.

Potassium bichromate gave no deposit; potassium nitrate and

carbonate, and ammonium nitrate and carbonate a light brown deposit: ferric hydrate.

Of special interest are potassium nitrate, ammonium nitrate and ammonium carbonate: all three give a corrosion, which is appreciable, but only a part of the theoretical, from 25 to 38 per cent., and all three show a sudden voltage rise during the run. It thus is safe to assume that with these three electrolytes the cells start active, but become passive during the earlier part of the run.

From these tests it seems to follow:

(1.) Potassium bichromate and potassium carbonate give the passive state of high voltage and no corrosion.

(2.) The chlorides and sulfates give the active state, showing the theoretical corrosion.

(3.) With potassium nitrate, ammonium nitrate and ammonium carbonate an active as well as a passive state may exist, and—in accordance with previous tests—the tendency is to change from the active to the passive state, and probably to start active. In the passive state the voltage is higher than in the active state, and the change from active to passive state is always accompanied by a considerable voltage rise.

(4.) Activity is always accompanied by the formation of the greenish-black ferrous compounds, which never appear during the passive state, but during the passive state only the yellowish-brown ferric compounds appear. At a change from the active to the passive state the ferrous compounds existing in the electrolyte, etc., are rapidly oxidized to ferric compounds.

It thus seems:

Iron in the ferric state is passive, in the ferrous state is active. Electrolytes in which ferrous compounds form, as chlorides and sulfates, give active corrosion. Electrolytes in which ferrous compounds do not form or can not exist, as bichromates, always give the passive state. Electrolytes of acids which give unstable ferrous salts, as the nitrates, may give the active as well as the passive state, but the tendency is towards the passive state; that is, even if the corrosion begins with the formation of ferrous compounds, these are oxidized to the ferric state, and then the activity ceases.

Possibly ferric hydrate is electro-positive towards iron, and thus, if once ferric hydrate appears on the positive plate, this

plate is protected, as the nascent oxygen then appears at the ferric hydrate and not at the iron; that is, the current issues from the former and not from the latter, and thus no corrosion occurs, as the iron is at a negative potential and thus protected.

Any solvent of ferric hydrate thus would destroy passivity.

Since some compounds, as bichromates and nitrates, tend to produce passivity, that is, protect the iron against electrolytic corrosion, while other compounds, as ammonium chloride, cause activity, that is, give full theoretical electrolytic corrosion, experiments were made to determine whether by the presence of passivating agents, bichromates and nitrates, iron can be protected from corrosion in the presence of activating compounds, as ammonium chloride, or, inversely, how large an amount of ammonium chloride is necessary to destroy the passivity given by bichromates and nitrates.

A run was made on five cells, containing a 1 per cent. ammonium chloride solution, to which was added in one cell 1 per cent., in another .1 per cent. of potassium bichromate, to the third cell 1 per cent., the fourth .1 per cent. of potassium nitrate, while the fifth cell contained only the 1 per cent. of ammonium chloride. The results showed, by the low voltage and the loss of weight, active corrosion throughout; that is, an amount of bichromate or nitrate, equal to that of ammonium chloride, does not reduce the active corrosion, has no protecting action yet.

A second test was made by using two cells with a 1 per cent. solution of potassium bichromate, the one containing in addition 1 per cent., the other .1 per cent. of ammonium chloride, and two cells with a 1 per cent. solution of potassium nitrate and the same amount of ammonium chloride. The results also showed active corrosion, equal to the theoretical amount and even slightly more, and low voltage on the cells.

Thus an amount of bichromate or nitrate, equal to 10 times that of ammonium chloride, does not yet give any protection against electrolytic corrosion, and, inversely, an amount of activating agent, equal to one-tenth of the passivating agent, destroys the passivity.

This second test was repeated by starting with excess current and with electrolyte containing only the bichromate or nitrate, so as to produce passivity at the start, and after starting the ammonium chloride was added. The voltage immediately

dropped and active corrosion began, and continued by the theoretical amount.

A series of tests was therefore undertaken to determine how small a quantity of activating agent is sufficient to destroy passivity. Four cells were made up, two with 1 per cent. potassium bichromate, two with 1 per cent. potassium nitrate solution, started with excess current, and run for some days. The high voltage and the absence of any visual attack showed passivity.

Then .01 per cent. respectively .02 per cent. ammonium chloride was added and the test continued for some days. The voltage remained high, and the iron passive. Then once more the same amount of ammonium chloride was added, giving a total of .02 per cent. respectively .04 per cent., or 1/50 respectively 1/25 as much as the amount of passivating agent. The bichromate cell with .02 per cent. NH_4Cl remained passive, but that with .04 per cent. showed some corrosion, and gave a lower voltage. The nitrate cell with .02 per cent. NH_4Cl retained high voltage, but showed slight corrosion, while the cell with .04 per cent. showed full activity, corrosion and low voltage. The plates were then taken out, weighed and put back and the run continued, except with the last cell, in which the iron plates had been eaten too far. This second run gave the same results. That is:

In a 1 per cent. potassium bichromate solution, .02 per cent. ammonium chloride does not yet give any corrosion, but .04 per cent. gives a slight, though appreciable, corrosion.

In a 1 per cent. potassium nitrate cell, .02 per cent. ammonium chloride gives a slight corrosion, .04 per cent. gives full activity.

Thus, 4 per cent. as much ammonium chloride as potassium bichromate, and 2 per cent. as much ammonium chloride as potassium nitrate, appear to be about the limit up to which passivity can be retained; that is, at this percentage an appreciable corrosion begins. Or, inversely, to protect the iron against electrolytic corrosion in the presence of ammonium chloride requires at least 25 times as much potassium bichromate, or 50 times as much potassium nitrate, as ammonium chloride.

Protection against electrolytic corrosion in the presence of very active corroding agents, as ammonium chloride, can not be produced by the addition of passivating agents, as bichromates and nitrates, except if excessive amounts of the latter are used.

As previous tests have shown that an extremely small per-

centage of chloride—.02 respectively .04 per cent. of ammonium chloride—is sufficient to destroy the passivity produced in a 1 per cent. potassium bichromate or nitrate solution, a corresponding test was made with ammonium sulfate.

Three cells were made up with a 1 per cent. potassium bichromate solution, and three cells with a 1 per cent. potassium nitrate solution. One of each kind was run without addition, as check cell, while to the other two various amounts of ammonium sulfate solution were added, giving percentages of ammonium sulfate from .01 per cent. to .66 per cent. (in addition to the 1 per cent. of potassium bichromate respectively nitrate). The cells were always started at high current.

The results showed passivity throughout; that is, .66 per cent. of ammonium sulfate does not yet destroy the passivity, while .04 per cent. ammonium chloride does, and the chlorides thus are many times more powerful activating agents than the sulfates.

Interesting to note is that in several instances some corrosion occurred in the potassium nitrate cell, and apparently this cell had started active, but soon became passive. The bichromate cell was always passive. Bichromates thus are more powerful passivating agents than nitrates.

Finally .02 per cent. and .04 per cent. of ammonium chloride was added to the cells containing respectively .33 and .66 per cent. of ammonium sulfate, and 1 per cent. of potassium bichromate respectively nitrate. The nitrate cells became active and gave complete corrosion, and the same also the bichromate cell with .04 per cent. chloride, while the bichromate cell with .02 per cent. chloride still remained passive, but gave a slight corrosion.

To investigate the effect of ammonium sulfate still further 12 cells were made up containing 1 per cent. ammonium sulfate and various percentages of potassium nitrate and bichromate.

The results were somewhat erratic, but in general showed that 1 per cent. and occasionally even .5 per cent. of nitrate or bichromate added to 1 per cent. of ammonium sulfate makes passivity possible under favorable conditions, as when starting at high current density, while activity tends to result from an interruption of current when the plates are in the electrolyte.

Thus the sulfates, while being activating agents, that is, com-

plete theoretical corrosion of the iron occurs in them, are very much less powerful than the chlorides, and from 50 to 100 per cent. of passivating agents, as nitrates or bichromates, are sufficient to produce passivity under favorable conditions, and a protection against them thus appears possible. Chlorides, however, are extremely powerful activating agents, and an extremely small percentage of them is sufficient to make passivity impossible; chlorides apparently are about 25 times as powerful as sulfates in destroying passivity.

To determine whether alkaline reaction of the electrolyte protects the iron against electrolytic corrosion, three cells were made up with a 1 per cent. solution of ammonium chloride and three cells with a 1 per cent. solution of ammonium sulfate. Of both kinds, one cell was left without addition, to the second was added 1 per cent. of slaked lime CaO_2H_2, to the third 1 per cent. of chalk powder $CaCO_3$.

The tests showed that $CaCO_3$ exerts no protective action, while CaO_2H_2 exerts a material protective action with ammonium sulfate, but very little with ammonium chloride; in the presence of CaO_2H_2 the electrolytic corrosion in ammonium sulfate is reduced to less than one-half (42 per cent. of the theoretical), and half of the voltmeter readings are high, half are low. Apparently the cell started passive, and became active after some time.

With ammonium chloride the reduction of corrosion by CaO_2H_2, equal in amount to that of the NH_4Cl, is only 6 per cent., hence almost no protective action yet.

To investigate the electrolytic corrosion which may be expected in iron in the ground, some tests were made with dirt solution as electrolyte, but the tests were not conclusive, and had to be postponed for lack of time.

The preceding investigation is very far from complete, and not too much reliance must be placed on the numerical values, for instance the effect of chlorides or sulfates on nitrates and bichromates, etc., as they are based on a small number of tests only, and a number of conditions, which are of influence, have not yet been studied, as the concentration of the electrolyte, the current density, the effect of circulation (which is possible in the solution of the electrolyte, but would be practically absent in the soil), the temperature, etc. However, some general conclusions appear warranted:

(1.) No conclusion can be drawn on the electrolytic corrosion of iron from the amount of current which passes from the iron as anode, since iron may assume a passive state, in which electrolytic corrosion is entirely absent, or an active state, in which the corrosion follows Faraday's law.

(2.) The conditions which lead to the active or to the passive state are not yet fully understood, but sometimes, under apparently identical conditions, either state may occur.

(3.) Alkaline reaction of the electrolyte, the presence of nitrates, and, more still, bichromates, tend to produce the passive state; sulfates, and especially chlorides, even in small quantities, produce the active state of electrolytic corrosion.

(4.) High current density, even if only momentary, tends to produce the passive state, absence of current the active state.

(5.) In the active state the products of corrosion are initially ferrous compounds, in the passive state ferric compounds, and the passive state occurs in such electrolytes in which ferrous compounds cannot exist or are chemically unstable.

(6.) In the passive state the potential difference at the electrodes is much higher than in the active state.

Balaklala Smelter and Cottrell Fume Controller. A. H. MARTIN. (*Mining Sci.*, lxiii, 337.)—The production of fine dust in the blast furnace is reduced to a minimum by treating only the coarse ore in the blast furnace, and the fines in the roasting and reverberatory furnace. The fumes are received in flue chambers and pass through the Cottrell fume controller to the stack. This controller consists of a series of positive electrodes which arrest the solid particles carried off by the gases. The steel electrodes are the positive poles of the plant and the negative poles are micanite rods. As the electric current leaps across to the negative micanite poles, the solids are deposited on mica saw teeth. An automatic jarring device causes the particles to fall into hoppers below.

Cost of Street Lighting by Gas and Electricity. H. T. LEE and D. STUART. (*Elect. Eng.*, vii, 165.)—The cost of lighting the streets in a number of places, including the cost of renewals, repairs and attendance, is stated in terms of the cost per candle-power per year. The figures vary greatly in different places, but the average seems to show that on the candle-power basis gas cost about 2½ times as much as electricity.

THE RÔLE OF WATER IN MINERALS.*

BY

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INTRODUCTION.

ALTHOUGH investigations of infra-red absorption spectra were begun about twenty-five years ago, it was not until the first years of the present century that an attempt was made to systematize the data previously obtained, and to publish it, as well as new data, in standard wave-lengths. This was due in part to the lack of knowledge of the optical constants (which prevented the calibration) of the prisms used, and to the difficulty in operating the spectroradiometric apparatus. To some the data seemed to be of passing interest, but of no great utilitarian value. To others the data seemed useless because of the question of the purity of the material used, and because of their not recognizing that the absorption spectrum of the impurity will be weak and will be superposed upon that of the substance in question.

The early experimenters were at variance as to whether the cause of the absorption bands is an inter- or intra-molecular phenomenon. If the cause is intra-molecular, then it ought to be possible to identify certain characteristic absorption bands with specific groups of atoms, or radicals, in the compound

* Extract from a paper to be published in the *Bulletin of the Bureau of Standards.*

under investigation. Now in the study of the carbon compounds, their constitution has been established by the replacement of certain constituents by organic radicals, by the preparation of a series of derivatives, by vapor density determinations, or by studying their physical properties in solution. Hence, following the example of the preceding experimenters, the writer turned to organic compounds for examples of substances having characteristic groups of atoms. Searching for further illustrations, groups of inorganic substances (*e.g.*, sulphates and nitrates) were examined. The chemical formulæ of minerals appeared to be written with such exactness that this seemed a rich field for material. But it was soon found that in mineralogy, which is essentially the chemistry of silicon compounds (see Myers's Mineralogy), it has as yet not been possible to apply any of the aforesaid methods used in organic compounds; that the constitution of many minerals has been derived indirectly from analogies with other compounds which are better understood, and that in many cases the constitutional formulæ are in doubt.

Being familiar with the older ideas in regard to the condition of water in crystals, it seemed easy to settle the question of inter-molecular action in causing absorption bands, by investigating substances containing *"water of constitution"*; but at the very beginning [1] it was found that this particular subject was in a more hopeless state of confusion than all the rest.

In the meantime, extensive investigations of all sorts of compounds proved conclusively that the important groups of elements, radicals, which are found in chemical compounds, have a definite effect upon radiant energy, especially upon low frequency, or so-called infra-red, radiation. This effect is manifested by intense absorption bands, the positions of which are characteristic of the radical or group of atoms causing these bands.

Hence, as a result of the application of these facts, it has come about that, instead of turning to chemistry and to other branches of physics to obtain evidence to explain the phenomena observed when radiant energy is passed through or is reflected from a substance, the problem is reversed and these

[1] Coblentz, *Physical Review*, 20, p. 252, 1905.

very phenomena are now applied to explain several conspicuous and intricate questions concerning the constitution of matter, and, in particular, the question of the manner in which water, or the constituents which form water, are combined in chemical compounds.

The investigation of water in minerals has been carried on at various times [2] during the past six years. The interest which Dr. Hillebrand has taken in this method of analysis has served to renew my interest in it and to further test its possibilities. After due consideration of the problem it was deemed best to renew the work by investigating opals having different amounts of water—from 3 to 8 per cent. After beginning the work it was found possible to decrease the water content of, and even to completely dehydrate, some specimens without seriously impairing their homogeneity. The material was selected from the collection in the United States National Museum. The water content was very kindly determined by Dr. Hillebrand, after which the cutting of the sections was done by the United States Geological Survey.

THE FUNCTION OF WATER IN SUBSTANCES.

The manner in which "*water of crystallization*" is held in minerals is not understood. By some it is considered to belong to the molecular structure; by others it is held that the molecules of water exist in their entirety among the other molecules, and hence belong only to the crystalline structure. It is a characteristic of water of crystallization that it is expelled from a mineral by very gentle ignition, always at a temperature far below red heat and frequently below 100° C.

In the case of *water of constitution,* the water is not supposed to exist as such in the mineral, but to result from the union of oxygen and hydrogen or from hydroxyl groups contained in the molecule. It is characteristic of this class of substances that they must be strongly heated, sometimes to a white heat, before they are decomposed and all the water is expelled.

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[2] "Water of Constitution and Water of Crystallization," Coblentz. *Physical Review,* 20, p. 252, 1905. *Physical Review,* 23, p. 125, 1906. *Bulletin, Bureau of Standards,* 2, p. 457, 1907. Jahrbuch Radioaktivität und Elektronik, 3, p. 397, 1907. *Physical Review,* 30, p. 322, 1910. Publication No. 65, Carnegie Institution of Washington, 1906.

The earlier writers held that in the case of crystalline substances the molecules of water exist in their entirety, whence the name "*water of crystallization.*" "The compounds containing water of crystallization are usually denied the title of atomic compounds, ordinarily applied to combinations of two or more elements in which the constituent atoms are associated in a single molecule, under the influence of the force which has received the name of chemical affinity, and in contradistinction are termed *molecular* compounds, being regarded as combinations of two or more separate molecules, *e.g.*, $CaSO_4+2H_2O$. This, although perhaps true of many compounds containing water of crystallization, is certainly not true of all, and notably the sulphates, which are deprived of their water of crystallization by heating to a high temperature."[3] The last molecule retained with such persistency was termed "*water of constitution,*" to distinguish it from water of crystallization. In many compounds the affinity seems different for the different parts of the crystal water. For example, ordinary alum $AlK(SO_4)_2+12H_2O$ gives off five molecules of H_2O at 100°, and five molecules at 120°, while the last two molecules remain until heated to 200°. In the same manner in the sulphate of magnesium ($MgSO_4+7H_2O$), Zn, Fe, Ni, and Co six molecules of water are given off at about 130°, while the last molecule of H_2O does not pass off until heated to 200° to 300° C. Examples of "*water of constitution*" are sugar, mica, and brucite, $Mg(OH)_2$, in which the O and H atoms are not united as H_2O, and do not unite to form water until sufficient heat is applied.

Various criteria have been set up (often based upon physical tests, refraction and polarization) by experimenters to distinguish between these various forms of water, but all seem unsatisfactory. For example, the fact that in certain crystals the water passes off at one, two, or three fixed temperatures, with a supposed change in homogeneity, has been considered evidence that the water is present as a definite compound. But the absorption and reflection bands of selenite ($CaSO_4+2H_2O$) show that it is a "double salt" or "molecular compound";

[3] Encyclopædia Britannica, 9th Ed., V, pp. 489 and 505. Graham-Otto Lehrbuch der Chemie, II, p. 173.

for the spectrum of selenite is the composite of the spectra of anhydrite, $CaSO_4$, and of water, H_2O.[4]

If selenite were a new compound, formed by the union of water and $CaSO_4$, then the (absorption and reflection) spectrum should be entirely different from that of the constituents, just as is true of mica. That some of these hypotheses are too narrow is shown by the fact that the absorption spectra of various substances such as selenite, opal, and the zeolites are identical as regards the position and intensity of the water bands. The water must therefore be present in the same manner in these two types of crystals; and since the absorption bands are identical with those of water in its free (liquid) state, it would appear that the temperature fixed point and vapor pressure tests are not a sufficient criterion for judging this question. If the water were chemically combined in selenite, then one would expect to find the absorption bands of water to be absent. It would appear just as tenable to consider the water occluded under a definite pressure, which raises its boiling point to a higher temperature. [As suggested by the writer some years ago, an investigation of the expansion (with change in temperature) of crystals containing water of crystallization, to learn whether there is a minimum such as obtains in water at 4° C., would be interesting.] Or we may liken the crystal unto a block built up of bricks and mortar. This analogy cannot extend very far, since an explanation is demanded: why in the one case the cement (water) crumbles at a definite temperature, while in other cases (zeolites) the phenomenon is progressive with rise in temperature.

It seems just as reasonable to assume that the water molecule can assume the same structure as the molecule of sulphate (or perhaps forms a film around the latter), and that the two crystallize in the same manner, thus building up a composite crystal just as is possible to grow a crystal of a mixture of alums.

That the hypothesis that water in crystals is united as a definite compound is based on a too narrow foundation is illustrated in the zeolites. They are crystalline compounds and the water is very loosely held. The water continues to be

[4] *Bulletin, Bur. Standards*, 2, p. 457, 1907. Carnegie Publication No. 65, pp. 18, 77, and 79.

gradually expelled as the temperature is raised, and it may be replaced by other substances, such as NH_3, H_2S, or C_2H_5OH. The dehydrated crystals absorb definite quantities of these substances as a sponge absorbs water, the process being accompanied by the evolution of heat. Since the amount of water present varies continuously with the vapor pressure, it is generally concluded that the water in the zeolites is not analogous to the water of crystallization of most hydrated salts, but resembles more nearly the intermixture which occurs in solid solution. In this case the hypothesis is tenable, for amorphous substances, *e.g.*, opal, which have similar absorption spectra, are also considered solid solutions; and in both groups of minerals the absorption spectrum of the hydrated material is the composite of water and of the anhydrous substance. But the vapor pressure criterion is not sufficient to judge minerals, as may be noticed from the experiments on tremolite. Here, too, the water is expelled gradually[5] with rise in temperature, and it was considered dissolved water; but no absorption bands of water are observable. The small bands at 2.9 μ may be due to hydroxyl groups, as inferred by Penfield and Stanley[6]; for in brucite, $Mg(OH)_2$, in diaspore, AlOOH, and in Göthite, FeO(OH), the 3 μ band is very weak,[7] as is true of the band in tremolite.

Turning from the crystals (*e.g.*, sulphate) which give off their water at one or more fixed temperatures to the zeolites, which are also crystalline substances, it is found, as mentioned on a previous page, that in the latter group of minerals the water is given off gradually between 100° and 400°. To explain this phenomenon it is supposed that the water is not chemically combined, but is present as solid solution. On this hypothesis the water should be present as such, and should give the absorption bands of water. As a matter of fact, as already mentioned, the zeolites do show the absorption bands of water; but so do the sulphates and other substances in which the water is expelled at a fixed temperature, indicating the sameness of the water in both groups. It is not clear to the writer why, if in some substances the water may be expelled at one fixed temperature and in another substance at several fixed temperatures,

[5] Allen and Clement, *Amer. Jour. Sci.*, 26, p. 101, 1908.

[6] Penfield and Stanley, *Amer. Jour. Sci.*, 23, p. 23, 1907.

[7] Publication No. 65, Carnegie Institution of Washington. *Bulletin Bur. Standards*, 2, p. 466, 1907.

it is not possible to have still other crystalline structures from which the water may be expelled at all temperature gradations, and yet have the water present in the same condition in all of them, as indicated by the radiometric tests.

THE CRITERION USED IN THE PRESENT METHOD OF ANALYSIS.

The criterion used in the present investigation for judging the condition of water in compounds is based upon the evidence deduced from extensive experimental data which shows that the absorption spectrum of a compound is *not* the composite of the absorption bands of the constituent elements. In this case the "physical molecule" has been changed. On the other hand, if the molecules (or the groups of atoms which cause the characteristic absorption bands) undergo no physical change when they combine to form a crystal (*e.g.*, selenite, $CaSO_4+2H_2O$), or when they enter into solution, then the absorption spectrum of the resultant combination will be the composite of the absorption bands of the constituents. Now this is the proposition that conflicts with some of the notions concerning definite chemical compounds. From the fact that there is a certain heat of hydration manifested in the formation of a crystalline substance (*e.g.*, hydrous sulphates), it is inferred that there is a new compound formed, when as a matter of fact the radiometric test shows that the water and the sulphate bands are just the same in magnitude and in position as they were before the constituents were united.

In judging the condition of water in minerals the main difficulty is in using substances which in the anhydrous state have no large absorption bands near the bands characteristic of water in its free (liquid) state. An excellent example is found in selenite ($CaSO_4+2H_2O$), which has an unusually large absorption band at 4.6 μ. This seemed to throw doubt upon the adequacy of the radiometric test until after the examination of anhydrite ($CaSO_4$) and other anhydrous sulphates, when it was shown that this large absorption band is characteristic of the sulphates. In the same manner the presence of OH groups in cane sugar confuses matters at 3 μ. So that the probability of cane sugar having a molecule of water of crystallization is based upon the evidence deduced from the presence of absorption bands at 1.5 μ and 4.75 μ, which coincide with the water bands at these points. The evidence not being very strong in

this case, the writer has never laid much stress upon it, in spite of the great similarity of the spectrum to that of other sugars having H_2O. In all the other examples previously described, the most superficial examination shows that the absorption bands of water in the various minerals are identical in magnitude and in position with those found in water in its free (liquid) state. Hence, in the present investigation, the criterion for distinguishing water of crystallization from water of constitution is the presence of absorption bands at 1.5, 2, 3, 4.75, and 6 μ, which is the location of the absorption bands of water. If there are no other absorption bands near by, then the intensity of these bands will be found similar to those of water, *viz.*, the bands at 1.5, 2, and 4.75 will be weak, while the bands at 3 μ and 6 μ will be very strong. Hydroxyl groups cause an absorption band at 3 μ, hence not distinguishable when present with water. Furthermore, the evidence for OH groups is not so clear-cut and definite as is found in water of crystallization. The intensity of the band seems to depend upon the activity of the OH group. For example, of the various hydroxides studied, the alcohols, etc., have a sharply defined band at 3 μ, while in brucite, $Mg(OH_2)_2$, and in several other minerals, the band at 3 μ is almost, if not entirely, wanting. In the alcohols, etc., the OH is more active, since it is replaceable by a metal (more acid) than the OH in brucite, which is not replaceable (more basic). Whether this is the true explanation of the phenomenon remains undetermined; and since the question of OH groups is of secondary importance in the present work, it need not be given further attention at present.

In passing it is of interest to note that substances containing the COOH or the C=O group have a very marked absorption band in the region of 5.8 to 5.9 μ. Silicates, as well as quartz, have a very small absorption band in the region of 2.9 μ, which is barely noticeable in the thin sections of minerals examined. Since the band is so weak, there is no danger of confusing it with the strong water band at 3 μ in opals.

In contrast with the other criteria, the radiometric test of the condition of water in minerals gives far more consistent results in classifying certain minerals. It is to be noticed, however, that this method of analysis shows no distinction between "*water of crystallization*" and "*dissolved water*" or "*water of solid solution.*"

In its behavior toward radiant energy, the molecule of water in crystals and in solid solution is identical with water in its free (liquid) state. This is, of course, in conflict with the commonly accepted notions concerning water of crystallization and water of solid solution; but it seems to be the only logical interpretation of the data obtained by the present method.

The main difficulty in this investigation is in obtaining substances which in the anhydrous state are free from absorption bands. This is practically impossible, since all substances have characteristic absorption spectra. Hence the best that one can do is to investigate various substances. Some give inconclusive evidence in one region of the spectrum (*e.g.*, cane sugar at 3 μ), while others confuse matters further in the infra-red (*e.g.*, the sulphates at 4.55 μ). Considered as a whole, however, the evidence is complete and convincing.

THE LEAST THICKNESS OF WATER DETECTABLE RADIOMETRICALLY.

This is about the first question asked in connection with the methods used in the present investigation.

On a subsequent page it will be shown that a given layer of water vapor is far more transparent than the same column when condensed into a liquid film; although the large absorption bands are found in both the liquid and in the vapor phase, the only difference being that of intensity. The film of water which is found on rock salt (prisms) does not cause absorption bands.

Whether the absorption bands of water are absent in substances which are more hydroscopic than rock salt (or in rock salt itself when exposed to very humid air) has not been determined. Furthermore, it must be shown that such a film of water is continuous.

It will be shown presently (see Figs. 6 and 7) that after dehydrating a certain sample of opal it absorbed water at the rate of about .06 per cent. (see Fig. 7B) per day. The various transmission curves are so widely separated that an increase in the water content amounting to one-third to one-fourth this value (or .02 per cent.) could easily have been detected. The thickness of the section of opal was .105 mm.; and, if .02 per cent. of it was water, the equivalent layer of water, if concentrated into a liquid film, would be about 3/100,000 mm. in thickness.

APPARATUS AND METHODS USED.

The apparatus used in the present investigation is essentially the same as used in previous work. The spectrum was produced by means of a 60° fluorite prism mounted on a spectrometer made of silvered mirrors 50 cm. in focal length. The spectrum was explored by means of a very sensitive vacuum bolometer, which is now being used in all radiation work requiring high precision. The period of the auxiliary galvanometer was only 4 seconds, which means a great saving in time when one considers that, in some of the earlier work, 1 to 1.5 minutes were required to make a single observation. The spectrometer slit and the width of the bolometer were 0.6 mm. wide or 4′ arc. A Nernst glower was used as a source of energy. An image of the glower was projected upon the spectrometer slit by means of a 15 cm. focal length silvered mirror. The crystal section was mounted in a holder directly in front of the spectrometer slit. The methods of observation consisted in (1) noting the galvanometer deflection when the crystal section was in the path of the light from the glower, and (2) noting the galvanometer deflection when the crystal section was not before the spectrometer slit. The ratio of (1)÷(2) gives the transmission in any given part of the spectrum; and it is simply a matter of setting the bolometer in different parts of the spectrum and noting the two galvanometer deflections. The method is analogous to spectrophotometric measurements, the bolometer being substituted for the eye. An accuracy of one part in 200 to 400 is easily attainable, which is more precise than is required.

The mineral sections were ground thin, but not highly polished. The size of the specimens was about 8 x 15 mm. They were mounted upon thick cardboard having rectangular openings cut therein. In this manner no light reached the spectrometer slit, except that which passed through the mineral section.

For further details in regard to apparatus and methods of observation the reader is referred to previous investigations of a similar nature.[8]

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[8] *Physical Review*, 16, p. 35, 1903. Publication, Carnegie Institution, No. 35, 1905; No. 97, 1908. *Bulletin Bur. Standards*, 4, p. 392, 1907.

SUMMARY OF PREVIOUS DATA.

In previous investigations of at least thirty-four substances, said to contain "water of crystallization," the one exception (aside from tremolite, which is included in the present paper) to the rule that such substances show the absorption bands of water was brucine ($C_{23}H_{26}N_2O_4+4H_2O$), which is an alkaloid having a complicated and unknown structure. An extensive examination of this compound failed to reveal any absorption bands of water. The transmission curve[9] has sharp bands at 1.7, 3.43, 6.86, and 7.3 μ which are to be found in all substances containing CH_2 and CH_3 groups. It has also a very large band at 5.95 μ (and 8.3 μ) which is to be found in all substances containing the C = O group. It is quite transparent throughout the infra-red. It is supposed to contain 16 per cent. of crystal water, which would be sufficient to cause a far greater opacity than observed radiometrically.

The list of minerals containing water of constitution included about a dozen samples of hydroxides, OH groups. As stated elsewhere, the absorption band of OH groups so characteristic of alcohols at 3 μ is often very weak, and sometimes it is entirely unresolved by the spectroscope. In serpentine there is a band at 3 μ which is very strong, and confirms the view that there are hydroxyl groups present in this mineral. The radiometric analysis also confirmed the view[10] that there are no hydroxyl groups in talc, in which there is not even a trace of an absorption band at 3 μ.

The one exception to the other methods of classifying the twenty-eight substances examined, containing water of constitution, is cane sugar, which is not supposed to have water of crystallization. As mentioned on a previous page, the evidence is not very strong; but there is sufficient similarity between the transmission spectrum of cane sugar and of other sugars having water of crystallization (there is no similarity with fructose, which has no crystal water) to suggest the presence of a molecule of water of crystallization.

It seems rather remarkable that out of a sum total of more than sixty substances examined radiometrically only two (per-

[9] Publication No. 65, p. 40, Carnegie Institution of Washington.
[10] Clarke and Schneider, *Amer. Jour. Sci.*, 40, p. 308, 1890.

haps only one) were found which did not agree with the other classification into water of crystallization and water of constitution.

GROUP I.—MINERALS CONTAINING WATER OF CRYSTALLIZATION.

Under this heading are described the characteristics of several crystalline and amorphous substances containing water. For, as already mentioned, the radiometric test finds no distinction between water of crystallization, absorbed water, or water in solid solution.

Water (H_2O).—In order to appreciate fully the significance of the data to be presented on minerals, it is necessary to describe the characteristics of water when examined in the liquid and in the vapor state. All observers [11] agree in their location of large absorption bands of water at the approximate wavelengths 1.5, 2, 3, 4.75, and 6 μ. All have found that water is extremely opaque to the deep infra-red radiation, so that the film had to be reduced to a few thousandths of a millimeter in thickness in order to be able to study it at all.

In fact, of all the substances examined, which included all the great groups of chemically related compounds, water stands unique in having a spectrum of numerous narrow absorption bands, which can be resolved only when the substance is reduced to a highly attenuated vapor. In the liquid state these groups of small bands coalesce into large bands, as indicated in Fig. 1. It is, of course, well known that a very thick layer of water is required to produce absorption in the visible spectrum.[12] The same is true for the infra-red region out to .933 μ (the "P" band in Fig. 2), but beyond this point the "general absorption" increases very rapidly, so that a layer of water 1 cm. in thickness absorbs all frequencies beyond 1.4 μ, and a layer .5 mm. in thickness causes complete opacity beyond 2 μ. The absorption of water for heat waves longer than 5 μ is so much greater than at 2 μ that a layer only .1 mm. in thickness causes complete opacity beyond 5 μ. Beyond 8 μ (to 50+ μ) water is quite transparent,

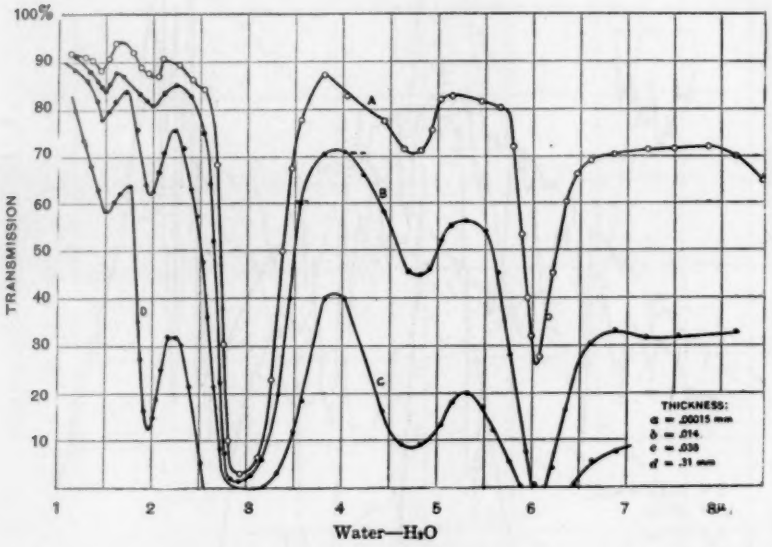
[11] Julius, Verhandl. Königl. Akad. Amsterdam. Deel I, No. 1, 1892. Paschen, *Ann. der Phys.* (3), 53, p. 334, 1894. Aschkinass, *Ann. der Phys.* (3), 55, p. 406, 1905.

[12] Abney and Festing, *Phil. Trans.*, 172, p. 887, 1882. Kayser, Spectroscopie, Vols. 2 and 5.

having no large absorption bands which would be useful in investigating the present problem.

The transmission curves of various thicknesses of water ($a = .00015$ mm.; $b = .014$ mm.; $c = .038$ mm.; $d = .31$ mm.) are given in Fig. 1. The cell, containing water, was made of two large, clear fluorite plates separated by tin foil. The various thicknesses were obtained by varying the number of layers of tin foil. For curve *a*, the thinnest obtainable platinum,

FIG. 1.



used in making bolometers, was inserted between the fluorite plates. The thickness of the platinum was computed from the electrical resistance and the surface dimensions of a bolometer strip. These curves show the great opacity of water at 6 μ as compared with the region of 1.5 and 2 μ.

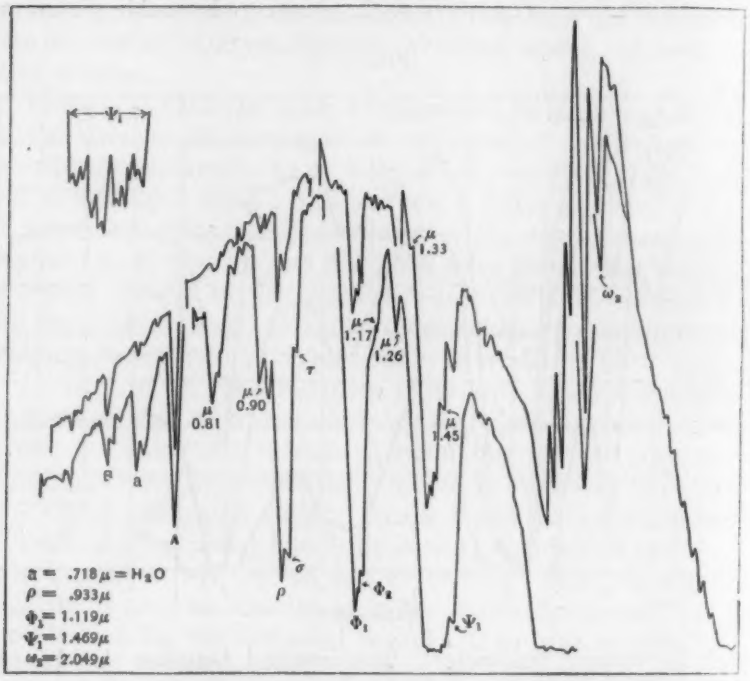
Angström [13] has shown that water vapor is more transparent than the liquid phase, when in such layers that the thickness is inversely proportional to the density. A familiar example is atmospheric water vapor, which transmits the sun's radiation [14]

[13] Angström, *Ann. der Phys.* (3), 39, p. 267, 1890; (4) 6, p. 163, 1901.

[14] Langley, Nat. Acad. Sci., 4, part 2, p. 197. Discussion in Carnegie Publication No. 97, p. 143.

to 11 μ, while a layer of water about two centimeters thick, which is equivalent to the water vapor in the earth's atmosphere (see Arrhenius Lehrb. der Kosmischen Physik), absorbs everything beyond 1.2 μ. The complexity of the absorption bands at 1.45 μ and at 2 μ, in Fig. 1, is shown in the spectrobolographic

FIG. 2.



Bolographic energy curves of the solar spectrum of a 60° glass prism.

curves [15] made at the Astrophysical Observatory. These curves are reproduced in Fig. 2. The upper curve, for Feb. 19, 1903, was made when there was but small water-vapor absorption. The lower curve, for Sept. 14, 1903, was made when the humidity was high and hence there was great water-vapor absorption. The rapid variation in intensity of the absorption bands is analogous to the observations in Fig. 1. A further

[15] Fowle, Smithsonian Misc. Coll., Vol. 47, No. 1468, 1904.

illustration of the complexity of the water bands is given in Fig. 3, which relates to the band at 6 μ in Fig. 1. Curve *a*,

FIG. 3.

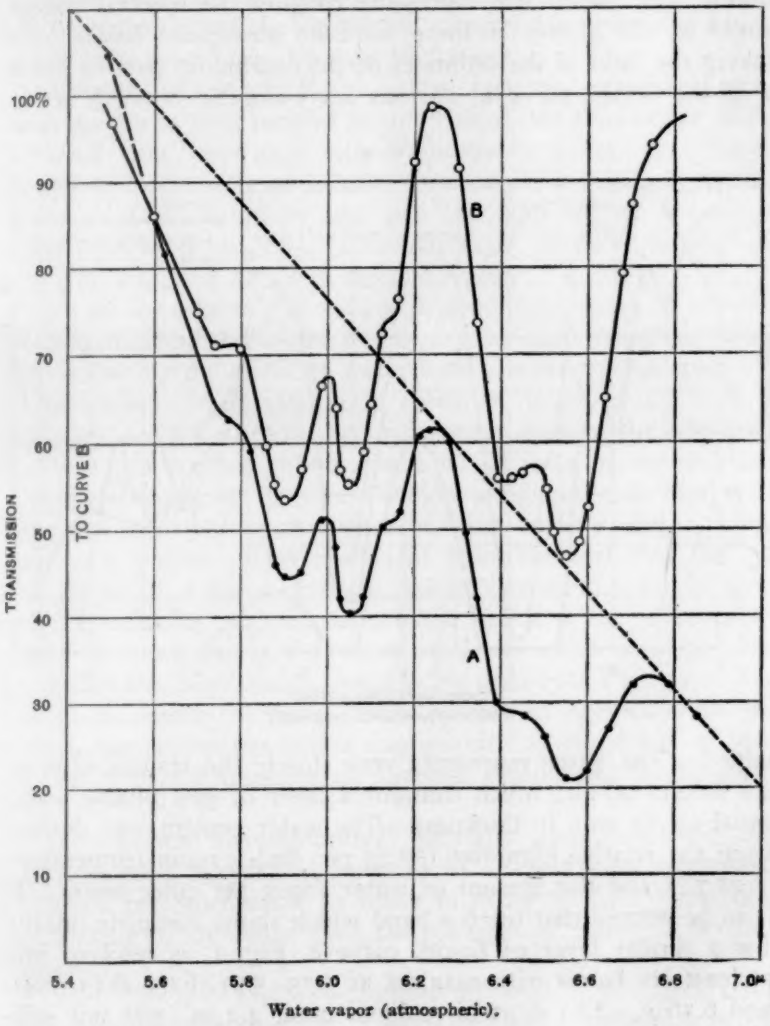
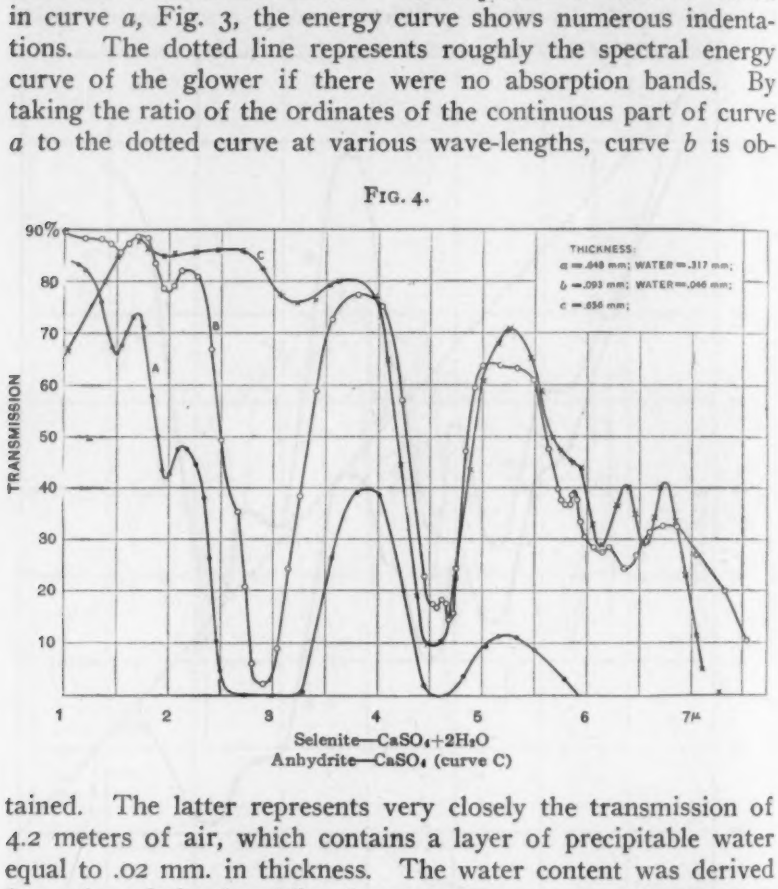


Fig. 3, was obtained by placing a Nernst glower at a distance of 4.2 meters from the spectrobolometer and projecting an

image of the glower upon the spectrometer slit by means of a large concave mirror. The spectral energy curve was then observed in the usual manner. When plotted to scale as shown in curve *a*, Fig. 3, the energy curve shows numerous indentations. The dotted line represents roughly the spectral energy curve of the glower if there were no absorption bands. By taking the ratio of the ordinates of the continuous part of curve *a* to the dotted curve at various wave-lengths, curve *b* is ob-

FIG. 4.



tained. The latter represents very closely the transmission of 4.2 meters of air, which contains a layer of precipitable water equal to .02 mm. in thickness. The water content was derived from the relative humidity (= 25 per cent.; room temperature = 21.7°) and the amount of water vapor per cubic meter. It is to be noticed that the 6 μ band which shows complete opacity for a similar layer of liquid, curve *b*, Fig. 1, is resolved into at least six bands with maxima at 5.75, 5.91, 6.05, 6.15, 6.41, and 6.56 μ. The short air column used, 4.2 m., was not sufficient to show the absorption bands of water vapor at 3 μ.

Anhydrite ($CaSO_4$).—The substance examined was a cleavage piece, split parallel to the *c* axis; thickness = .656 mm.

The transmission curve, *c*, Fig. 4, of this mineral shows small absorption bands at 3.75, 5.75, 6.15, and 6.55 μ; a very large band, at 4.55 μ, is due to the So_3 ion, and is characteristic of sulphates. This mineral was investigated previously, and is included here to illustrate the great difference in the opacity of the hydrous and the anhydrous mineral (see curves *a* and *c*, which have practically the same thickness).

Selenite ($CaSO_4+2H_2O$).—The sections examined were cleavage pieces split parallel to the *b* axis; the thicknesses being $a=.648$ mm., $b=.093$ mm. respectively (Fig. 4). Since twenty-one per cent. of selenite is water, the thickness of the water, if free, would be 48.8 per cent. (sp. gr. of selenite is 2.33; $2.33 \times 21 = 48.8$) of the thickness of the specimen, or $a=.317$ mm. and $b=.046$ mm. of water.

Of all the minerals investigated, containing water of crystallization, this and the following one are the most conspicuous for demonstrating the effect of water upon the absorption spectrum of substances. The absorption bands of water at 1.5, 2.0, 3, 4.75, 6.0, and 6.5 μ are very conspicuous in spite of the anhydrite bands which confuse matters at 6 μ. It is to be noticed that a layer of water in its free (liquid) state, curve *d*, Fig. 1, is far more opaque than an equivalent layer, curve *a*, Fig. 4, when held in a crystal. This is evident from the fact that the .31 mm. layer of water is entirely opaque beyond 2.5 μ. In fact, the transmission spectrum of selenite indicates the presence of water in more nearly the vapor state, in which it is possible to resolve the large bands into smaller ones (see Fig. 3). This change in density of water in the process of crystallization involves energy changes which may require consideration in connection with the question of thermal equilibrium in dehydration.

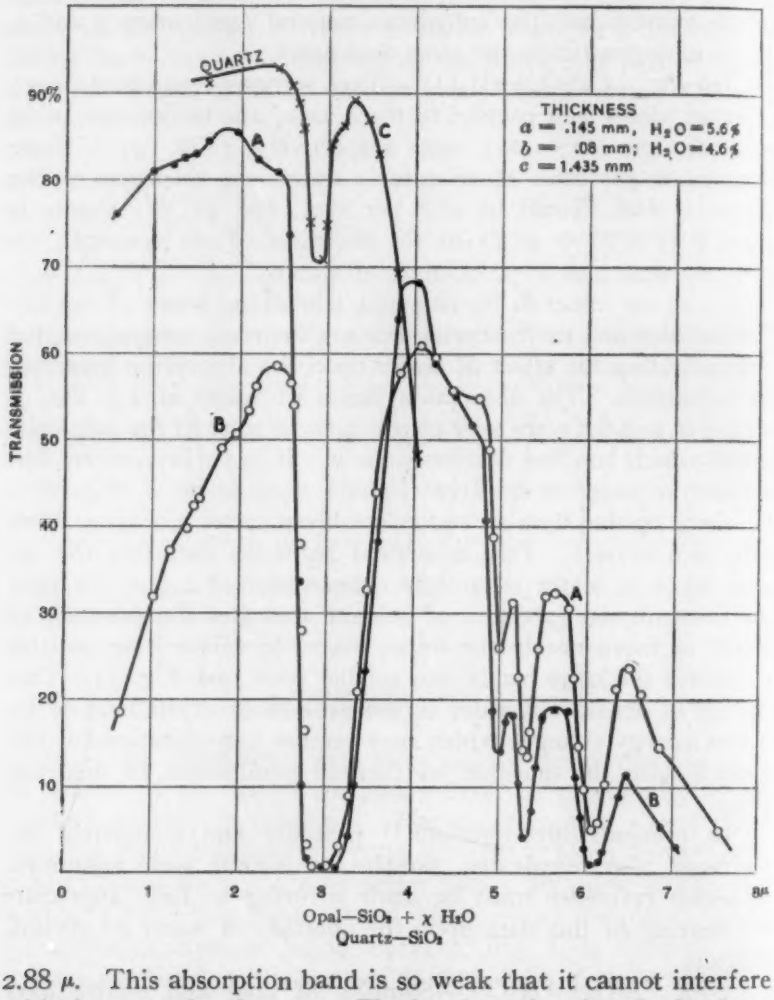
In previous investigations [16] partially and completely dehydrated, also rehydrated, samples of selenite were examined, to which reference must be made in order to fully appreciate the bearing of this data upon the question of water of crystallization.

Opal (SiO_2+XH_2O).—Samples of opal and quartz have been examined previously.[16] Quartz has small absorption bands at 2.9, 4.35, 5.02, 5.3, 6.0, 6.26, and 6.65 μ. The band at 2.9 μ

[16] *Bulletin, Bur. Standards*, 2, p. 457, 1907. Carnegie Publication No. 65.

is barely observable in a section .1 mm. in thickness. Curve *c*, Fig. 5, gives the transmission of a section 1.435 mm. in thickness, cut perpendicular to the optic axis. The maximum lies at

FIG. 5.



2.88 μ. This absorption band is so weak that it cannot interfere with the water band at 3 μ. The bands at 6 and at 6.26 μ form a composite with the water band at 6 μ, of which the maximum appears at 6.1 μ. The group of atoms in quartz is very strong

and maintains its characteristics, more or less sharply defined, in the various silicates investigated.

Opal (amorphous quartz) contains variable proportions (2 to 30 per cent.) of water. It shows no traces of crystallization. Opal is considered a solid solution, for the water contained is a function of the vapor pressure.

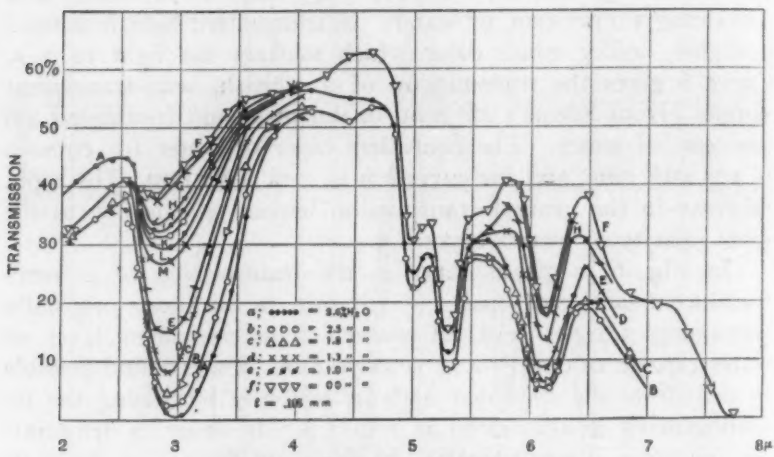
The transmission curve of opal has the general outline [16] of the curve for water and contains the bands of water at 1.5, 2, 3, 4.75, and 6 μ. The latter is complex, as mentioned above.

For the present work the samples of opal were not perfectly transparent, which caused a scattering of the rays shorter than 2.5 μ. In Fig. 5, curve *a* gives the transmission of a sample of opal (from Queretario, Mexico) .145 mm. in thickness, and containing 5.6 per cent. of water. In transmitted light it showed a slightly milky white color which scatters the light to 2 μ. Curve *b* gives the transmission of a whitish, semi-translucent sample (from Silesia) .08 mm. in thickness and containing 4.6 per cent. of water. The equivalent layer of water for curve *a* is, t = .018 mm., and for curve *b* it is, t = .0077 mm. The rapid decrease in the general transmission beyond 4 μ is due to the great opacity of quartz beyond 3 μ.

In Fig. 6 is given, curve *a*, the transmission of a semi-translucent sample of opal, t = .105 mm. in thickness, originally containing 3.6 per cent. of water. The equivalent layer of water (sp. gr. of opal = 2.1) is .0079 mm. It was found possible to dehydrate the specimen without seriously increasing the inhomogeneity, as illustrated at 2 to 3 μ. In order to dehydrate the specimen, it was necessary to dismount the section from its cardboard support and place it in a porcelain tube, which was then heated with a Bunsen flame or blast lamp. The specimen was weighed before and after heating, and knowing the water content before heating it was possible to compute from the loss in weight the water remaining after heating. For example: starting with the section weighing 32.037 mg., the loss in weight was .360 mg. The original water content was 3.6 per cent., from which it was computed that for curve *b*, Fig. 6, the water content was 2.5 per cent. The weighings were made by Mr. W. C. Bishop, whose long experience in such work insured both speed and high accuracy. The weighings were made on an assay balance taking a maximum load of 1 gram. The working

sensitivity was 1 mg. = 10 divisions; probable error of a single weighing .002 to .005 mg. It was found that the weighings became constant in less than ten minutes after dehydration. It will be shown presently that this specimen absorbed about .06 per cent. of water per day. Since the weighings were completed and the specimen was remounted within 15 minutes after dehydration, and since the observations on the absorption band at 3 μ were completed within 45 minutes after heating the specimen, this question of reabsorption (so frequently asked by all comers) needs no further consideration. Curves *c*, *d*, and *e* were ob-

FIG. 6.

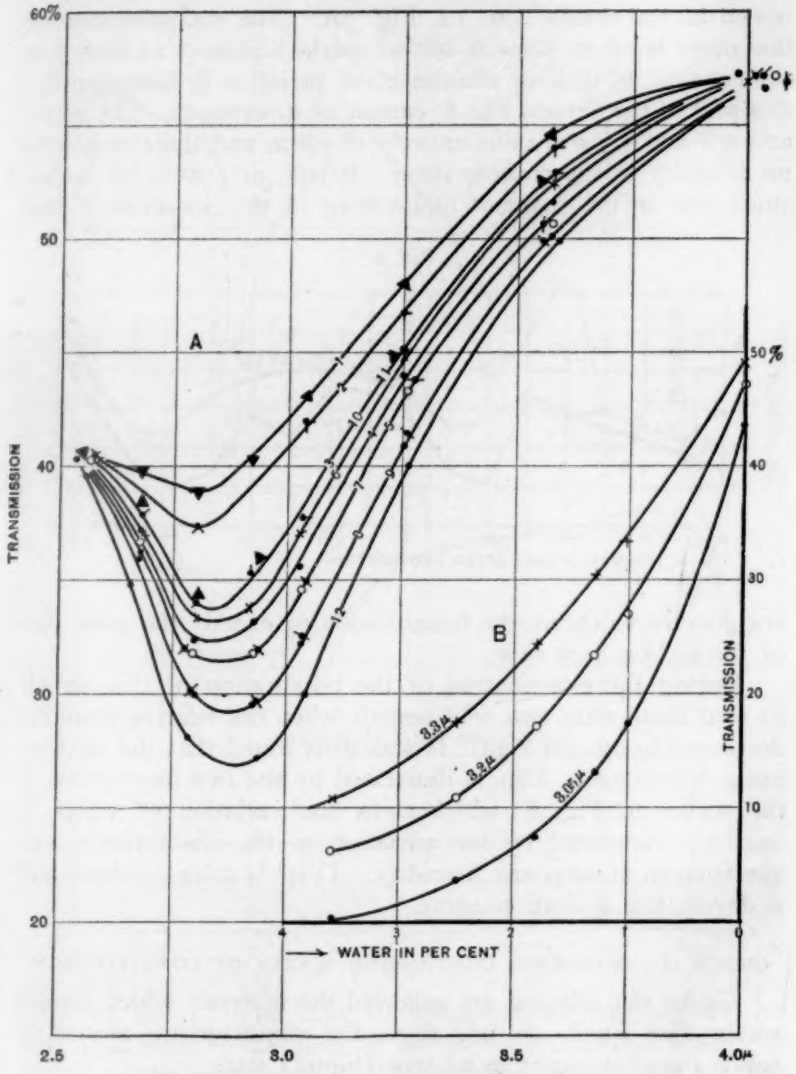


Opal in various stages of dehydration.

tained in the same manner as curve *b*. Each time the section was dismounted there was a slight loss due to breakage, so that after obtaining curve *e* the specimen was placed in a platinum receptacle and heated to a bright red (700°) for one hour. It was then mounted permanently upon the cardboard support and on examination gave curve *f*, Fig. 6. The small band at 2.9 μ remains; but whether it is due entirely to SiO_2, or whether it still represents a trace of water, remains undetermined. After standing over night it reabsorbed moisture, giving curve *g*. Two days thereafter the transmission had fallen to curve *h*. This examination of the reabsorption of water was continued for seventeen days after dehydration, the relative humidity of the

laboratory being determined daily by means of a ventilated hygrometer. The daily variation of the absorption band at 3 μ

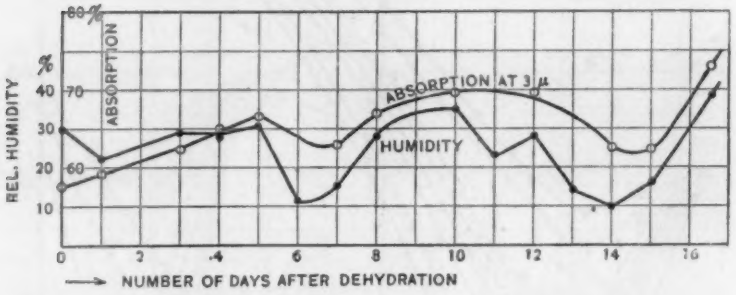
FIG. 7.



is shown in Fig. 7A, which represents curves *f*, *g*, . . . *m*, Fig. 6, on a different scale. The numbers attached to the various curves

indicate the order in which they were observed. In Fig. 7B are given several isochromatic transmission curves, obtained from curves *a*, *b*, *c*, *d*, and *e* of Fig. 6. From these curves it is possible to obtain a rough estimate of the water content represented in the curves 2 to 12, Fig. 7A. The disappearance of the water band at 6.1 μ is not so marked as at 3 μ; but it is evident that, in making allowance for variation in homogeneity, this part of the curves, Fig. 6, cannot be superposed. The bands at 5.0 μ and 5.3 μ are due entirely to silica, and there would be no difficulty in superposing them. It will, of course, be understood that in the frequent remounting of this specimen it was

FIG. 8.



not possible to obtain the transmission of exactly the same part of the section each time.

During the examination of the rehydration of this sample of opal there were two cold periods when the relative humidity decreased to ten per cent. It was then found that the opal became dehydrated. This is illustrated by the two depressions in the curves in Fig. 8, which show the variation of water in opal (as measured by the variation in the absorption) with variation of atmospheric humidity. There is a lag of about half a day in the hydration curve.

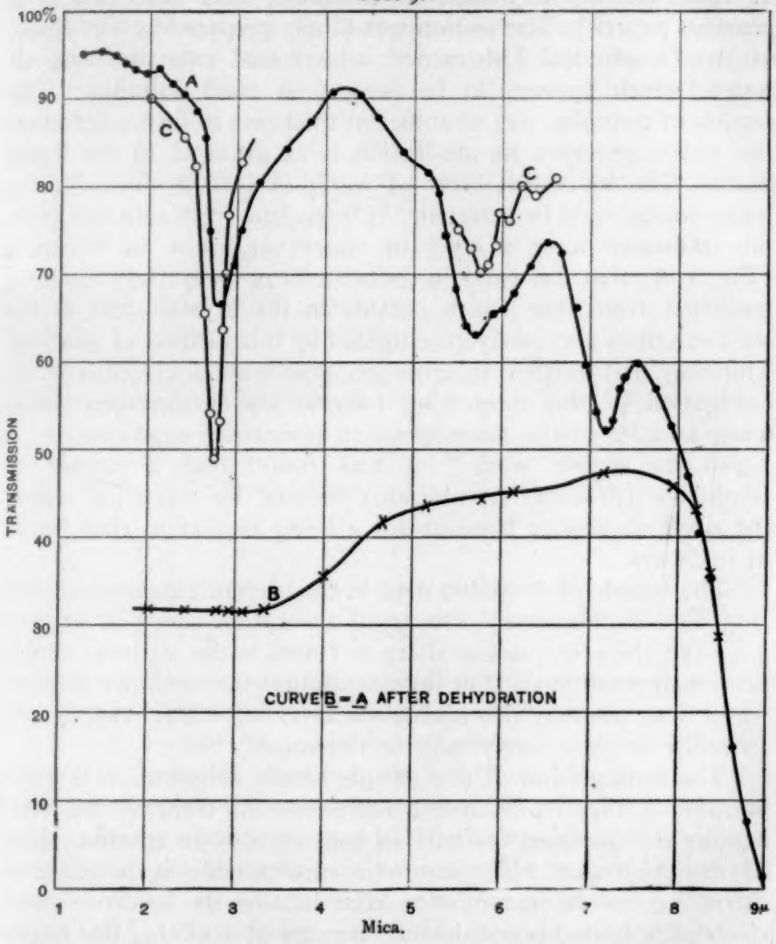
GROUP II.—MINERALS CONTAINING WATER OF CONSTITUTION.

Under this heading are collected the minerals which contain water, but which do not show the characteristic absorption bands found in water in its free (liquid) state.

Muscovite Mica ($H_2KAl_3(SiO_4)_3$).—The transmission spectra are given in Fig. 9. Curve *a* was obtained with a rock

salt prism, while curves *b* and *c* were observed with a fluorite prism. The thickness was .04 mm. Curve *b* shows the transmission of the specimen after dehydration. The absorption bands are common to silicates; and none are in common with

FIG. 9.



those of water. The band of selective reflection beyond 9 μ does not seem to be affected by the constitutional water, as should be the case, since it is known that these bands are due to the SiO radical. The other bands disappear on dehydration, as they should, since on dehydration only the constituent oxides

remain. The layer of mica is too thin and the inhomogeneity is too great to show the weak absorption band of silica at 2.9 μ. A more complete list of minerals containing water of crystallization is given in previous communications [16] on this subject.

Tremolite ($CaMg(SiO_3)_4$).—The transmission of a section of this mineral, 0.23 mm. in thickness, was described in a previous paper.[17] The section was kindly prepared by Dr. Allen, of the Geophysical Laboratory, who found two per cent. of water, which appears to be present in solid solution. The section of tremolite was of sufficient thickness to insure detecting the water, provided its absorption is as great as in the liquid phase. The equivalent layer of water was .0138 mm., but no water bands could be detected. It is evident from this and from the transmission of a layer of water .014 mm. in thickness (Fig. 1, *b*) that the water in tremolite is in an entirely different condition from that which obtains in the crystals and in the solid solutions previously investigated by this method of analysis. Thinking that further information would be disclosed, the investigation of this interesting mineral was undertaken anew, using samples of the same specimen previously examined.

In the earlier work [18] it was found that a sample of amphibole (probably hornblende) showed no traces of water, the small absorption band at 2.9 μ being similar to that found in feldspars.

The sample of tremolite used in the present examination was .095 mm. in thickness. The small absorption bands at 2.9 and 3.2 μ are, therefore, not so sharp as found in the .23 mm. sample previously examined. On the assumption that two per cent. of water was present, the equivalent layer of water (sp. .gr. of tremolite is 3) is .0057 mm. in thickness.

The transmission of this sample before dehydration is given in curve *a*, Fig. 10. Curve *b* represents the transmission after heating the specimen for half an hour at 200° in an atmosphere of dry hydrogen. The curve is superposable upon curve *a*. Curve *c* gives the transmission after heating the specimen in an electrically heated porcelain tube furnace at 500° for five hours. In this case the absorption band at 2.9 μ is practically destroyed.

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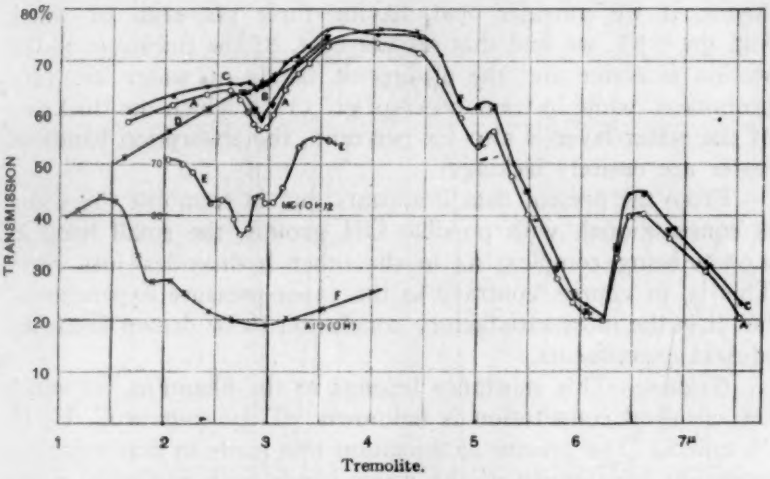
[17] *Physical Review*, 30, p. 326, 1910.

[18] Carnegie Publication No. 65, p. 64.

Curve *d* gives the transmission after heating the specimen in the electric furnace at 925° for five hours. The transmission curve is identical with curve *c*, showing that most of the chemical change was brought about at 500°.

In the dehydration the specimen became slightly inhomogeneous, which caused a scattering of the radiation to 3 μ. The band at 2.9 μ has entirely disappeared, showing that it belonged to the compound that existed before dehydration. The bands at 5 and 6 μ have undergone no change. They belong to

FIG. 10.



anhydrous silicates; and the general outline of the transmission curve is not unlike that of the feldspars.[18]

In Fig. 10 are also given the transmission curve of brucite, $Mg(OH)_2$, and of diaspore, $AlO(OH)$. The brucite curve shows a complex region of absorption bands at 2.5, 2.75, and 3.0 μ. The 3 μ band is found in substances having OH groups. In diaspore the absorption is very complex and the individual bands, which no doubt exist, are not resolved. Bauxite, $Al_2O(OH)_4$, and Göthite, $FeO(OH)$, also have wide bands at 3 μ.

The chemical composition of amphiboles, of which tremolite is a species, does not appear to be definitely known, some[3] arriving at the conclusion that the water is present as " dissolved

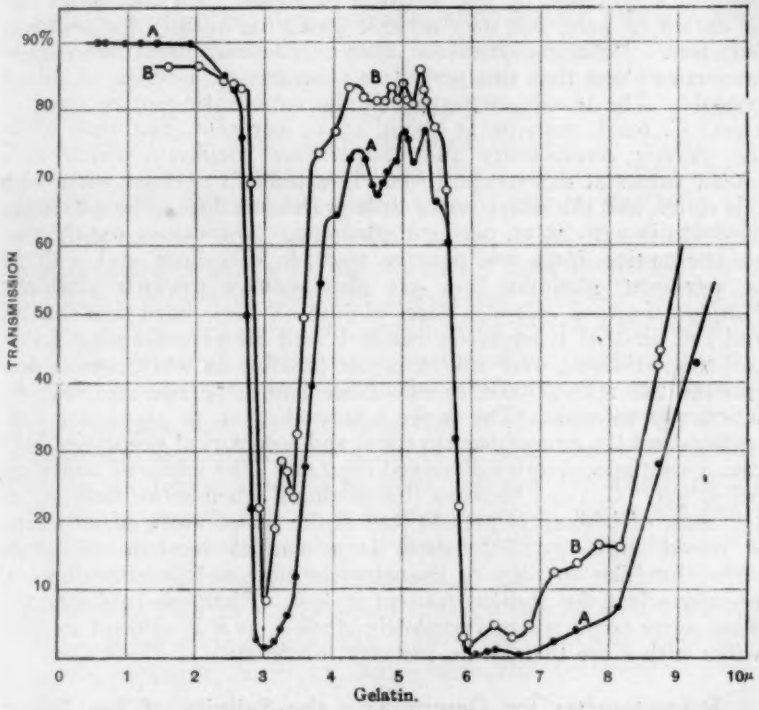
water," while others [6] considered the water to be present as hydroxyl groups combined with Al_2O_3 and Fe_2O_3. From the present data it is evident that the water in tremolite is not present in the same condition as in other substances containing water in solid solution or dissolved water. Attention has already been called to the fact that in selenite the density of water is much less than in the free state, so that a layer of water equivalent to .31 mm. transmits radiation to 6 μ, while a film of water .31 mm. in thickness is completely opaque beyond 2.5 μ. The "density" of water in opal is far less than in selenite, but its opacity is of the same order of magnitude. Again, if we consider opal, having three per cent. of water (sp. gr. = 2), we find that six per cent. of the thickness of the section is water and the absorption bands of water are very prominent, while in tremolite (sp. gr. 3), in which the thickness of the water layer is also six per cent., the absorption bands of water are entirely lacking.

From the present data it appears that in tremolite the water is constitutional, with possible OH groups, the small band at 2.95 μ being complex, as in the other hydroxides just cited. This is, of course, contrary to the vapor-pressure experiments; but it is the most satisfactory conclusion to be drawn from the present experiments.

Gelatin.—This substance belongs to the albumins, of which the chemical constitution is unknown. They contain C, H, O, N, and S. The present examination was made to determine the variation in intensity of the water bands with variation in the water content. The film was .025 mm. in thickness, and it was perfectly clear. Curve *a*, Fig. 11, gives the transmission curve before dehydration, and curve *b* gives the transmission after partial dehydration, the film being tinged a faint light brown. The peculiarity of these curves is the absence of absorption bands at 1.5 and 2 μ. The general appearance of the transmission curve is entirely unlike that of water and of substances containing water. The absorption bands are sharp and narrow, as usually found in carbohydrates. In fact, the whole curve appears as though the water were present as "water of constitution," the sharp band at 3 μ being due to OH groups. The 3.4 and 6.8 and 7.3 μ bands are characteristic of substances rich in CH_2 and CH_3 groups. The very sharply banded region of great opacity at 6 to 8 μ is characteristic of carbohydrates con-

taining NO_2 groups. There are absorption bands at 2.4, 3.0, 3.43, 4.0, 4.6, 4.9, 5.15, 5.5, 6.0, 6.8, 7.3, and 8.1 μ. This conclusion that the water in gelatin is constitutional, instead of being held as is water in a sponge, is in agreement with the notions held by several chemists with whom the writer has discussed this data. Furthermore, the conclusion, arrived at four or five years ago, that cane sugar contains water of crystal-

FIG. 11.



lization (or water present in a similar manner, whatever name we choose to give it) is no longer so antagonistic to the views held as to the condition of the water present in this sugar.

In conclusion, it may be added that this method of analysis is entirely different from any of the others heretofore employed. While nothing very marked can be claimed for it at present, it has served the purpose of giving us a clearer understanding of the rôle of water in substances, and of indicating errors in the conclusions arrived at by other methods.

Electrical and Mechanical Properties of Alloys of the Noble Metals. W. GEIBEL. (*Z. Anorg. Chem.*, lxx, 240.)—*Palladium-silver alloys.*—The existence of a continuous series of mixed crystals is confirmed and the curves expressing their mechanical and electrical properties correspond to those of the *palladium-gold* series. The minima for electrical conductivity, temperature coefficient, and thermo-electro-motive force, occur at 40 at. per cent. silver, and the maximum tensile strength at 50 at. per cent. silver. The temperature coefficient is extremely small at the minimum. The negative value of the thermo-electro-motive force of palladium towards platinum is augmented by the addition of silver. All the alloys can be drawn to wire, but they occlude gases too readily for practical purposes. *Palladium-platinum alloys.*—Electrical and mechanical properties show that this series also consists of a series of mixed crystals. The tensile strength and thermo-electric-motive force at 1200° C. reach maxima at about 45 at. per cent. platinum, while the electric conductivity and temperature coefficient reach their lowest values at this composition. It is difficult to draw wires with this series, and the alloys are of little practical value. The maximum hardness is with 45 at. per cent. platinum. The values for thermo-electric-motive force are positive towards palladium and with 10 at. per cent. platinum they are also positive towards platinum. *Platinum-iridium alloys.*—Pure iridium is very hard and brittle, and the limit of hardness is reached with alloys containing 40 at. per cent. iridium; over this it is not possible to work. With less iridium the alloys have excellent mechanical properties and are practically valuable. The series was studied up to 35 at. per cent. iridium and the curves for electrical and mechanical properties indicate a continuous series of mixed crystals. The effect of annealing below 750° C. is to increase the hardness when more than 10 at. per cent. of iridium is present, but if the temperature of annealing is raised above 750° C., there is a marked decrease of tensile strength. The ductility of the wires is increased by annealing, especially when the iridium content is low. *Platinum-gold alloys.*—This series could not be completely studied, as it is difficult to draw wires with more than 20 at. per cent. platinum.

Refractometer for Determining the Salinity of Sea Water. A. BERGET. (*Comptes Rendus*, clii, 984.)—As it is hardly possible on board ship to determine the salinity by the density measurement by areometers, the total reflection refractometers of Pulfrich and of Abbe were tried. A simplified Féry refractometer was found more convenient. The determination is rapid and only a few cubic centimetres of water are required. Experimenting with known solutions of sodium chloride, the salinity increasing by 0.005 from 0.005 to 0.045, the refractive index rose from 1.333804 to 1.34050 at 16° C., according to a law following a straight line; experiments with diluted sea-water were found satisfactory.

COMPOSITION OF AMERICAN COMMERCIAL GLUCOSE AND STARCH SUGARS.*

BY

A. HUGH BRYAN,

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THE complete hydrolysis of starch yields the sugar d-glucose, or, as it is commonly known, dextrose. The hydrolysis is supposed to proceed by steps, various intermediate products being formed. These have often been enumerated as soluble starch, maltose and various dextrins. The more complete the conversion of starch, the more d-glucose is formed; the less complete, the more of the intermediate products, which we usually call dextrin. In the United States the starch almost wholly used is from the Indian corn or maize. Some potato starch is used, but only on a very small scale; while in other countries the potato furnishes almost all the starch for these products.

On a commercial scale this conversion is carried on in large copper boilers, or kettles, the starch being mixed with water and acid in weighed proportions and heated under pressure for varying lengths of time. The usual acid in this country was formerly sulphuric, but now hydrochloric acid is the one almost wholly employed. By varying the quantity of acid, the pressure (and thereby the temperature of boiling) and also the length of time of heating, almost any stage in conversion of the starch can be reached. By suddenly reducing the pressure and quickly cooling at any desired stage, the conversion can be stopped. Thus products of varying composition can be made, and in commerce we find these varying products. They are known as commercial glucose, 70 sugar, 80 sugar, and commercial dextrose.

COMMERCIAL GLUCOSE.

This is a thick, viscous liquid never showing crystallization. In its production the time of conversion is short, so as to yield more of the intermediate products than of d-glucose. After conversion the thin liquor is neutralized with soda, filtered, and

* Read at 2d International Congress of Alimentary Hygiene and Rational Feeding of Man, Brussels, Oct., 1910, and published by permission of the Secretary of Agriculture.

concentrated by evaporation under low pressure to a thin syrup of about 30° Baumé. Then it is run through bone char and finally evaporated to the desired consistency in vacuum pans. This consistency is expressed in degrees Baumé—so we have from 42° glucose up to 45° glucose, the varying densities being adopted for different uses to which it is put. The color of the commercial glucose varies from water white to brown, although the white products predominate.

Of the 28 samples given below, 26 are made from corn and 2 from potato starch. The methods of analysis used are as follows:

Moisture: Refractometer and Geerlig's table. [1]

Reducing Sugar: The Munsen and Walker method and tables [2] were used for this determination. An aliquot portion of the solution used for polarization was employed.

Ash: Five grams of the material were ashed at low heat in a platinum dish in a muffle. The ash after weighing was dissolved in water and the per cent. insoluble determined.

Polarizations: Thirteen grams of the glucose were weighed out, dissolved in water, and made up to 100 c.c. Powdered dry kaolin was added and shaken, then the whole filtered. A polarization was made immediately and again after standing 24 hours. The temperature of polarization was 20° C. Fifty c.c. of the solution was transferred to a 100 c.c. flask, 5 c.c. of hydrochloric acid added, and the whole allowed to stand at room temperature 24 hours for inversion. Polarizations on the invert solution were made at 20° C. and at 87° C. A polarization of the direct solution was also made at 87° C.

The results are given in the following table. Averages have been made for each determination and also the maximum and minimum figures. For comparison the averages and means of 10 samples of German glucose and 6 of American glucose, made by Herzfeld, [3] have been added.

Moisture: The average moisture content is 16.47 per cent., with extremes of 20.00 and 11.95 per cent., the variation being due to the concentration of the syrup, some of these samples having a density of 43° B. and others 42° B. The German glucose average is 19.7 per cent.

[1] *Intern. Sugar J.*, 10, 69–70.
[2] *J. Amer. Chem. Soc.*, 1906, 28, 663.
[3] *Zeit. des Vereins Deut. Zuckerind.*, 1907, 44, p. 614.

Reducing Sugars: The average figure for this determination is 35 per cent., with extremes of 39.56 per cent. to 30.21 per cent. With a content of much above 40 per cent., it is claimed that crystallization is liable to occur. The German glucoses show a much higher reducing sugar content, viz., average 40.7

TABLE I.

	Ser. No.	Water	Dextrose	Ash	Undetermined	Total	Polarization					
							Direct			Invert		
							20°	87°	87° 1.0315	20°	87°	87° 1.0315
		%	%	%	%	%						
	7420	13.20	37.36	.57	48.87	100.00	181.1	173.5	179.0	180.0	171.4	167.8
	7075	11.95	35.05	.51	52.49	100.00	184.3	176.6	182.2	183.2	174.0	179.5
	7069	13.95	37.27	.56	48.22	100.00	180.0	171.8	177.2	179.6	169.8	175.2
	7421	16.85	35.43	.57	47.15	100.00	173.5	165.2	170.4	172.8	163.0	168.1
	7378	16.75	33.49	.91	48.85	100.00	175.5	168.9	174.2	174.8	166.2	171.4
	7376	16.60	38.49	.30	44.61	100.00	165.8	158.7	163.7	165.0	156.0	160.9
	7086	15.80	38.03	.45	45.72	100.00	169.0	161.0	166.1	168.4	159.2	164.2
	7085	15.35	38.25	.47	45.93	100.00	173.0	162.6	167.7	172.0	161.8	166.9
	7082	16.55	32.05	.60	50.80	100.00	181.8	172.5	177.9	181.2	169.2	174.5
	7081	17.85	33.20	.70	48.25	100.00	175.5	166.9	172.4	174.8	166.8	172.1
	7076	16.30	32.38	.51	50.81	100.00	179.0	170.4	175.8	178.4	167.6	172.9
	7068	16.20	35.56	.43	47.81	100.00	173.4	167.4	172.7	172.8	162.4	167.5
	7067	16.20	37.16	.63	46.01	100.00	175.0	167.8	173.1	174.8	163.4	168.6
	7065	15.85	37.10	.67	46.38	100.00	175.3	167.3	172.6	173.8	164.8	170.0
	7048	16.40	35.15	.59	47.86	100.00	175.4	166.6	171.9	174.6	164.6	169.8
	7047	15.95	34.77	.60	48.68	100.00	175.6	167.9	173.2	174.8	164.8	170.0
	7422	18.60	36.18	.44	44.78	100.00	169.5	161.3	166.4	167.8	158.6	163.6
	7087	16.35	33.05	.50	50.10	100.00	178.4	170.2	175.6	177.4	168.4	173.7
	7379	19.90	33.95	.79	45.36	100.00	166.0	159.1	164.1	166.0	158.0	163.0
	7084	20.00	39.12	.42	40.46	100.00	155.8	150.0	154.7	155.6	146.4	151.0
	7083	15.95	38.95	.39	44.71	100.00	169.1	162.7	167.8	168.6	159.8	164.8
	7077	18.95	30.21	.58	50.26	100.00	174.8	167.1	172.4	174.0	160.2	165.3
	7070	16.95	34.03	.59	48.43	100.00	173.2	165.3	170.5	172.0	165.0	170.2
	7066	18.50	37.43	.40	43.67	100.00	167.9	160.9	167.0	166.0	158.0	163.0
	7045	16.45	31.46	.46	41.63	100.00	181.6	171.0	176.4	180.4	171.6	167.0
	7046	16.95	31.69	.50	50.86	100.00	179.6	169.9	175.2	178.8	167.6	172.9
	5348	15.60	38.00	.24	46.16	100.00	170.0	162.2	167.3	169.0	160.0	165.0
	7377	15.10	39.56	.29	45.05	100.00	171.0	164.3	169.5	170.8	162.8	167.9
Average (28)	.....	16.47	35.51	.52	47.14	100.00	173.9	166.0	171.34	173.1	163.6	168.7
Maximum	.....	20.00	39.56	.91	52.49	100.00	184.3	176.6	182.16	183.2	174.0	179.5
Minimum	.....	11.95	30.21	.24	40.46	100.00	155.8	150.0	154.72	155.6	146.4	151.0
Herzfeld-German, glucose—												
Average	.....	19.7	40.7	.267	.....	100.00	161.6	.....	.....	154 7	.....	.....
Maximum	.....	20.4	47.4	.404	.....	100.00	181.2	.....	.....	161.2	.....	.....
Minimum	.....	18.0	36.5	.179	.....	100.00	149.6	.....	.....	138.4	.....	.....
Herzfeld-American, glucose—												
Average	.....	18.7	35.8	.419	.....	100.00	170.6	.....	.....	168.8	.....	.....
Maximum	.....	20.1	38.8	.675	.....	100.00	177.0	.....	.....	174.0	.....	.....
Minimum	.....	17.4	33.3	.249	.....	100.00	160.6	.....	.....	159.2	.....	.....

per cent. and extremes of 47.4 and 36.5 per cent., and were these figures calculated to moisture-free basis, there would be a much wider variation.

Ash: The average figure for this determination is 0.52 per cent., with extremes of 0.91 and 0.24 per cent., by far the larger number, however, ranging around the average figure. The German glucoses show a much lower figure, viz., 0.26 per cent.

average and 0.404 to 0.179 per cent. extremes. This would indicate one of two things: either a larger per cent. of acid is used in the United States or more ash is present in the starch from corn than from potatoes.

Undetermined: No attempt has been made to precipitate the dextrins by alcohol and weigh them, although a study will be made of this later.

Polarizations: Comparison of direct polarization made immediately and on standing 24 hours showed no muta-rotation. The d-glucose evidently is not present in percentages large enough to give this. The results of the immediate polarization are not given in table.

DIRECT AT 20° AND 87°.

The polarizations at 20° average +173.9° V, with extremes of +184.3° V and +155.8° V. For the German glucose the average is +161.6° V, with extremes of +182.2° V and +149.6° V, lower figures than for the American glucoses. When polarizing these solutions in a jacketed tube at a temperature of 87° C. and calculating the reading obtained by the factor 1.0315[4] (100 c.c. of solution at 20° =103.15 c.c. at 87°), there is noted a decrease in the direct polarization, viz., an average of +171.34° V and means of +182.16° V and +154.72° V. In this reading the temperature of the wedges was still 20° and the only change was the temperature of the solution.

INVERT AT 20° AND 87°.

The invert polarization at 20° averaged +173.12° V, with extremes of +183.20° V and +155.60° V. The differences between these figures and those at 20° on direct readings are very small, showing little decomposition of the commercial glucose by the cold inversion method used. The readings made at 87° on the invert solution after correcting for change in volume show a greater decrease from the reading at 20° than was noted in the direct readings at the same temperature, viz., +168.7° V average and extremes of +179.5° V and +151.0° V. This is no doubt due to some decomposition taking place when heating to 87° in the acid solution. With the German glucose, the invert readings average +154.7° V, wth extremes of +161.2° V and

[4] Bur. of Chem., U. S. Dept. of Agr., Bull. No. 110, p. 17.

+138.4° V. The method of inversion for these figures is not given in the article referred to, but on account of the great differences between the direct reading at 20° and the invert at 20°, viz., average +6.9° V, there must have been some decomposition. However, in Herzfeld's figures for American glucoses, this difference is not so great, averaging +1.8° V; possibly there are present in German glucose substances that are more easily broken down by the acid than those in American glucoses.

STARCH SUGARS.

Three distinct grades of sugars are produced. Wagner[5] gives the following average composition of these:

Determinations	70 Sugar	80 Sugar	Anhydrous* sugar
Water	19.7%	11.2%	4.0%
D-glucose	70.2	79.9	94.6
Dextrin	9.3	8.0	0.7
Ash	0.8	0.9	0.7
Total	100.00	100.00	100.00

* In the opinion of the writer this should be commercial dextrose.

It seems evident, then, that the 70 and 80 refer to the percentage of d-glucose present. By some "70 sugar" is known as "Brewer's sugar" or "Nabob," while "80 sugar" is known as "Climax" or "Acme." These two sugars, while microscopically crystalline in structure, are placed on the market in an amorphous mass somewhat similar in appearance to soap, the former being much lighter in color than the latter. The dextrose is generally in a fine powder, rarely in large crystals.

The sugars result from a more complete conversion of the starch, either from longer and higher treatment or from the use of more acid. After conversion the liquid is neutralized, boiled in evaporators to a desired density and then passed over bone black. The next treatment is concentration in a vacuum pan to the point of crystallization. The product is then allowed to cool for this to take place. In case of dextrose, this cooled product is subjected to further treatment for purification. Some 18 samples of these sugars were examined and may roughly be divided into two classes—crystalline sugar in small granules or

[5] *J. Soc. Chem. Ind.*, 1909, 28, 347.

balls, such as dextrose, and cake sugars. The latter is again divided into 70 and 80 sugars. The methods of analysis were as follows:

Moisture: By drying to constant weight at 70° C. in vacuum on sand.

Dextrose: Same procedure as in commercial glucose analysis.

Dextrin: About 2 grams of the material were dissolved in 10 c.c. of water in a 200 c.c. flask by heating. After complete solution, the flask was cooled and absolute alcohol added to the 200 c.c. mark with shaking. The mixture was corked and allowed to stand for settling of the precipitate. After this had occurred, the clear liquid was poured off, the precipitated dextrins were washed with 95 per cent. alcohol, water was added and the precipitate dissolved and washed into an ordinary tared moisture dish. The water was evaporated off over steam bath and the dish and contents heated to constant weight in a vacuum oven at 70° C. The weight of the precipitate was thereby determined. The dried precipitate was again dissolved and its reducing sugar content determined in the usual way. The above weight was then corrected for the weight of the d-glucose found and the percentage of dextrin thereby calculated.

Ash: In same manner as for commercial glucose.

Polarization: Ten grams of the material were dissolved and made up to 100 c.c. Dry powdered kaolin was added and shaken, then filtered. The solutions so prepared were allowed to stand for 24 hours to come to constant polarization. The reading so obtained was multiplied by 3.284 (the factor for normal weight of dextrose when polarizing a 10 per cent. solution).

The first three sugars show little variation in composition, but the ash of two is higher than that of the other one. The d-glucose by polarization is higher than by reduction, but in two cases the results agree fairly well. The next three sugars show a rather even composition. Their appearance was the same, but obtained from different makers and in different sections of the United States. The water content of these was about double that of the first three and the d-glucose content about 9 per cent. lower. The per cent. of undetermined matter is much larger than in the former class.

The two samples of 80 sugars show a rather even composition. The percentage of d-glucose varies only about 0.6 per cent. and the moisture content only 1.5 per cent. The ash is much higher than that of the samples just discussed, and the per cent. of undetermined also has increased.

The 70 sugars do not show a very even composition. The d-glucose varies from 66.6 per cent. to 73.16 per cent. The per-

TABLE II.

Ser. No.	Appearance	Water	Dextrose	Dextrin	Ash	Undetermined	Total	Polarization	
								10g to 100cc	Dextrose 32.84*
		CRYSTALLINE SUGARS.							
		%	%	%	%	%	%	°V.	
6998	Cream granulate	5.04	90.70	.52	.97	2.77	100.00	28.65	94.08
7026	Cream granulate	5.10	89.96	.16	1.06	3.72	100.00	27.70	90.96
7019	Cream granulate	5.67	89.36	.54	.48	3.95	100.00	28.00	91.95
7012	Balls small.....	9.57	82.68	.31	.62	6.82	100.00	27.50	90.31
7009	Balls small.....	9.94	81.52	.37	.64	7.53	100.00	27.70	90.96
7000	Balls small.....	9.21	83.76	.44	.64	5.95	100.00	27.80	91.30
		CLIMAX OR 80							
7007	D'k yellow cake.	10.61	77.24	1.15	1.17	9.83	100.00	28.40	93.20
7029	D'k yellow cake.	9.06	77.84	.96	1.18	10.96	100.00	26.50	87.03
		NABOB OR 70							
6999	L't yellow cake.	13.77	72.32	.57	1.08	12.26	100.00	26.15	85.88
7006	L't yellow cake.	16.55	67.46	1.45	.95	13.59	100.30	30.30	99.50
7011	L't yellow cake.	15.66	70.64	.60	.94	12.16	100.00	26.30	86.37
7024	L't yellow cake.	16.65	70.12	1.24	.47	11.52	100.00	30.30	99.50
7025	D'k yellow cake.	15.76	73.16	.81	.97	9.30	100.00	25.10	82.43
7027	L't yellow cake.	17.33	66.72	2.42	.45	13.08	100.00	33.45	109.85
7001	L't yellow cake.	18.03	69.70	.65	1.00	10.60	100.00	24.90	81.77
7005	L't yellow cake.	17.74	70.12	.67	1.12	10.35	100.00	28.45	93.42
7028	L't yellow cake.	17.63	66.60	.94	.48	14.35	100.00	32.50	106.73
7023	L't yellow cake.	15.20	71.28	2.32	.52	10.68	100.00	32.00	105.09

* The normal weight of dextrose polarizing 10 grams to 100 c.c. is 32.84 grs.

centage of dextrin in two samples is much higher than in the other cases, being over 2 per cent. Dextrose by polarization in three cases gives over 100 per cent. This comes about from the presence of a large quantity of the intermediate products of starch conversion having high specific rotatory power. The undetermined matter has increased a little over that present in the 80 sugars. This, of course, is to be expected, as in the 70 sugars conversion has not been carried as far as in 80 sugars and there exists a larger percentage of these intermediate products.

Treatment of Sulphated Storage Cells. G. A. PERLEY. (*J. of Phys. Chem.*, xv, 489.)—When a lead accumulator is neglected lead sulphate forms over the surface of the plates, while the capacity of the cell drops towards, or even as low as, zero. Various methods of renovation have been proposed, and the conclusions as to their merits are: (1) A badly sulphated cell can be restored by charging at the normal rate in a sodium sulphate solution. (2) It is desirable, but not necessary, to use lead "dummies" outside the end plates. (3) The concentration of sodium sulphate may be varied within wide limits, but 200 grams of the crystallized salt per litre are recommended. (4) The sodium sulphate must meet the requirements as to purity which are prescribed for battery acid. (5) The cost of electrical energy to restore a 40 ampère hour cell should not exceed 10c. (6) Since sodium sulphate is not deleterious to the cell, it is not necessary to wash the solution completely out of the pores of the plates. (7) It has been stated that a cell can be restored by charging at half the normal rate for a long time in the regular battery acid; but it is probable that the time and electrical energy required would be excessive in the case of very badly sulphated cells.

Magnesium. ANON. (*Eng. Min. J.*, xcii, 12.)—The consumption of magnesium in the United States in 1910 was no greater than in 1909, the total value being about $12,000. This metal seems destined to have a much wider use in the future, as magnesium is of greater value than aluminum for refining steel; and also because great interest is now being aroused in the remarkably light and strong alloys produced by the proper admixture of small amounts of zinc with magnesium. These alloys are stronger than aluminum alloys and have a specific gravity of about 1.8 as against 3.0 for the lightest commercial alloys of aluminum. It is reported they are extensively used in aeroplane manufacture. Alloys of magnesium with 2 to 4 per cent. of zinc can be wrought and rolled, and have a fracture like fine steel. They can be readily cast and turned, like brass or copper, without the use of soap or petroleum and they resist the action of air and water. Considering that bulk for bulk magnesium can be manufactured at less cost than aluminum, it will necessarily become a strong competitor of the latter metal wherever great lightness is desirable. The price now is $1.25 per 1 lb., but it is expected to come down to 50c. in the near future.

Manganese Bronze. ANON. (*Iron Age*, lxxxviii, 2, 93.)—The Committee of the American Society for Testing Materials is of opinion that the term "manganese bronze" should be applied to metal conforming to the following limiting analysis: Copper 55 to 60 per cent., zinc 39 to 45 per cent., iron not over 2 per cent., tin not over 2 per cent., aluminum 0.5 per cent., manganese 0.5 per cent. This is a proposed standard definition on which the Society has not yet voted.

AN EXPERIMENTAL STUDY OF VORTEX MOTIONS IN LIQUIDS.

BY

EDWIN F. NORTHRUP, Ph.D.,

Palmer Physical Laboratory, Princeton University.

(Concluded.)

PHOTOGRAPHY OF VORTEX RINGS.

THE problem which was presented of photographing fluid vortices proved to be one of very great difficulty. It was, indeed, over a year after the first attempt at solution before a satisfactory one was found. In the beginning the facilities available were inadequate and interruptions were frequent during the course of the experiments.

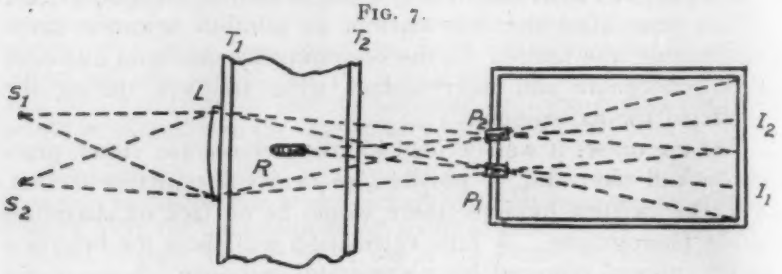
At the outset it was decided to take stereoscopic views, practically full size, and, if possible, so nearly instantaneous that, with the swiftest motions, there would be no lack of sharpness in the photographs. A little calculation will show the briefness of the interval required for a successful exposure. Some of the negatives were made from rings moving at the rate of 20 mm. in 1/80 of a second. If the photograph is to show clear and sharp under a lens no part of the ring should move over 1/20, or certainly not over 1/10 mm., during the time of an exposure. Hence the exposure should not last longer than from 1/16,000 to 1/32,000 of a second.

No mechanical shutter could be constructed to give so short an exposure. At first this fact was not fully appreciated, and a few preliminary trials were made in which a steel shutter moved by a powerful spring was used. Views were obtained, but the delicate details were all absent. It was then rightfully concluded that the photographs must be made with an electric spark, which preferably should not last over 1/50,000 of a second. As the intensity of the light must be great in proportion as the time of exposure is reduced, and as the light must pass through 12 cm. of water besides two plates of glass and at least two lenses, it was necessary to devise means of obtaining a light of very great intensity and quantity.

In photographing falling drops of a liquid, as was done so

beautifully by Worthington, the time of fall through a given height in air could be depended upon as fairly constant. The reproducibility of the speed of the vortex rings could not, however, be so depended upon. Experiments showed that it was impossible to so exactly regulate the force of the blow on the diaphragm of the gun and other necessary conditions that the velocity of the rings could be relied upon to be twice quite alike. All difficulties, except the last, were overcome, and this proved not to be serious in the end. The optical method employed giving complete success, and which I think could not be improved upon, was as follows:

FIG. 7.



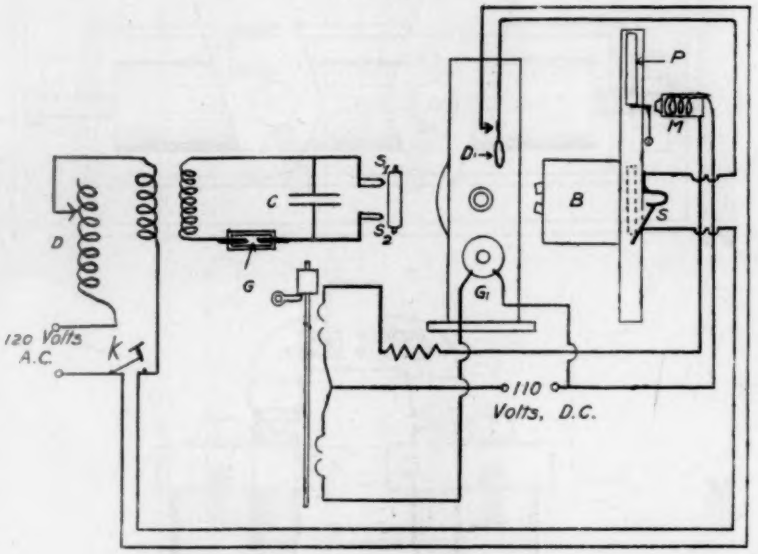
A plano-convex lens, L, (Fig. 7) 12.5 cm. in diameter, was held in a frame against one of the glass sides of the tank. The lenses, p_1 and p_2, of the stereoscopic camera were placed as shown in the diagram, 25 cm. from a plane midway between and parallel to the sides of the tank. The camera was adjusted to give a focus at 25 cm. The two stereoscopic images of the ring R would thus appear full size upon the photographic plates. Two sources of light, s_1 and s_2, were located back of the lens in such positions that the image of s_1 was focussed on the lens p_1 and the image of s_2 on the lens p_2. This arrangement projected upon the camera plates I_1 and I_2, two brilliant circular disks of light of uniform brightness. The ring thus appeared in the camera as a dark object against a brilliantly lighted background.

If a suitably moving photographic plate and the vortex ring R are as indicated, when instantaneous flashes simultaneously occur at s_1 and s_2 stereoscopic negatives are secured. A variety of makes of photographic plates 3½ by 6½ inches were tried. The most rapid plate tried was the Lumiere-Sigma, but Seed plates and Eastman plates also gave satisfactory results.

Methods of producing strong flashes of light at s_1 and s_2 received considerable study and experimentation before a satisfactory one was hit upon. The arrangement finally employed is shown in Fig. 8.

A generator of several kilowatts capacity supplied alternating current of forty cycles at 120 volts to the primary of a transformer having a transformation ratio of 1/100. In the circuit with the primary of the transformer there was a variable

FIG. 8.

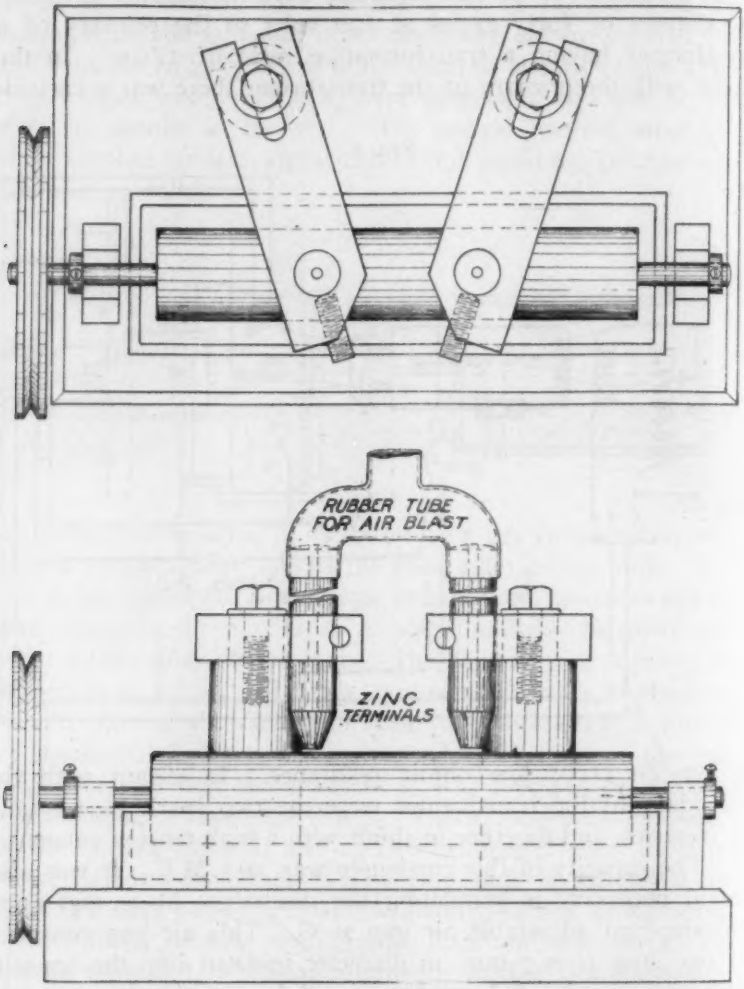


inductance D of low ohmic resistance. In circuit with the secondary of the transformer were the two spark gaps s_1 and s_2, in series, and together in shunt with a high tension condenser C. The capacity of this condenser was .013 M.F. It was also found necessary in regulating the discharges at s_1 and s_2 to introduce an adjustable air gap at G. This air gap consisted of two steel rods 7 mm. in diameter inserted into the opposite ends of a porcelain tube and separated from each other, near the centre of the tube, by about 1 cm.

The problem was to make such adjustments that only one discharge would occur at the air gaps s_1 and s_2 during the time

of each alternation of the generator current, or 80 discharges per second. It was arranged to have the dropping photographic plate P fall in 1/80 of a second through a distance equal

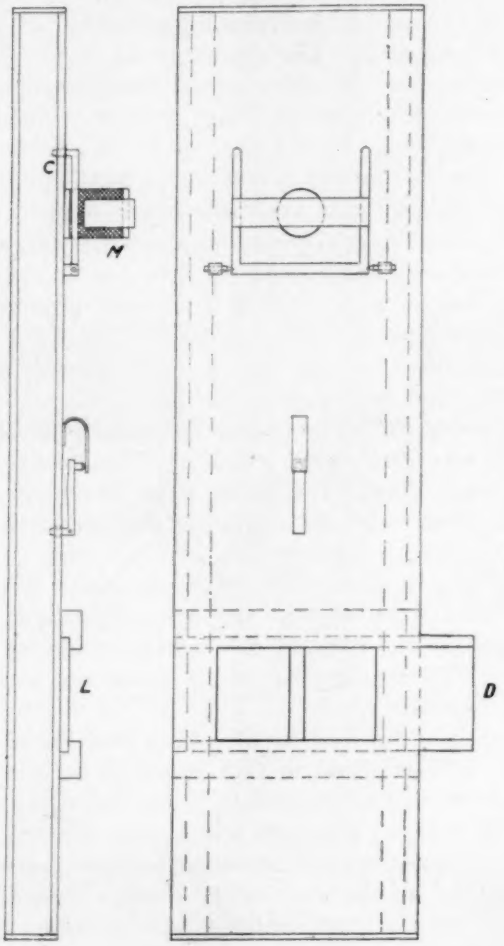
FIG. 9.



to the diameter of one of the illuminated areas on the plate. Thus two successive illuminated areas on the plate would touch, tangent to each other, and not overlap. If the plate were a

long one, three or four round disks of deep black (in the negative) would be photographed upon it during its passage past the back of the camera box B. If the ring happened to be in

FIG. 10.



the field of view while the plate was passing the camera box, two, three, or even four views, 1/80 of a second apart, might be secured.

The design of the spark gaps s_1 and s_2 was carefully worked

out to give necessary uniformity in the discharges, as well as the greatest possible brilliancy and actinic power to the light.

The construction of this double discharge gap is shown in Fig. 9. It consists of three essential parts, a trough of mercury, a rotating cylinder of brass dipping into the mercury, and two upright rods of zinc to which the high-tension terminals of the transformer are joined. The discharge takes place between the amalgamated ends of the zinc rod and the amalgamated mirror-like surface of the rotating brass cylinder. The parts were made sufficiently large to run quite cool. A small motor maintained the brass cylinder in rotation at a moderate speed. It is thought an air-blast as shown in the figure would have been an improvement as tending to steady the discharge and keep it more regular. It too frequently happened that, due to inability to hold conditions constant, two or more discharges occurred during a half cycle and negatives were spoiled.

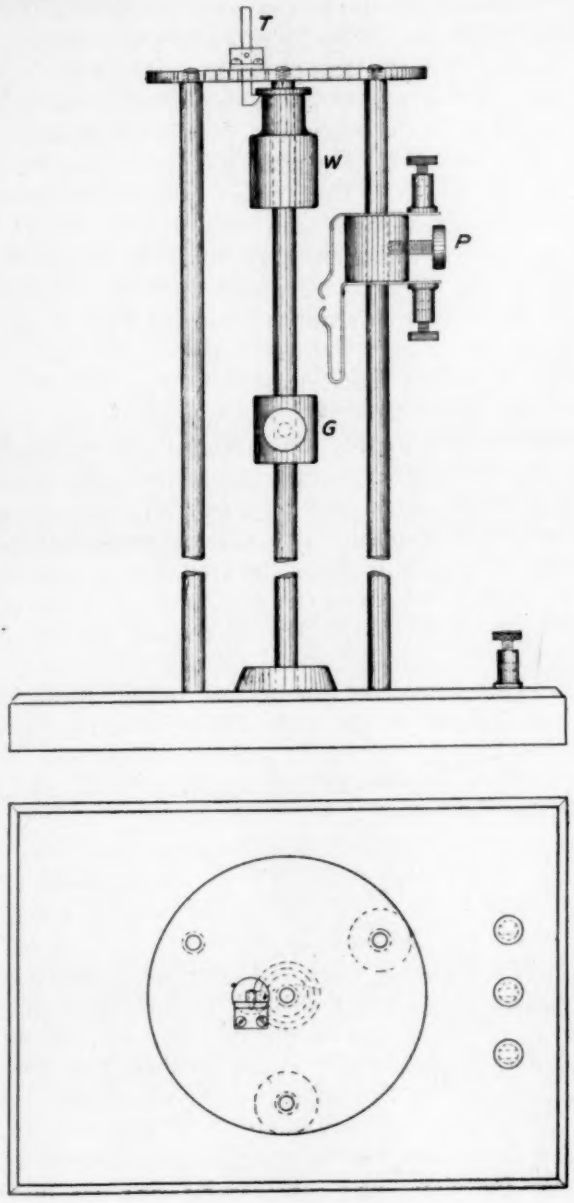
The plate slide is plainly shown in the general view, Fig. 3, and in more detail in Fig. 10.

As two plates had to be dropped at exactly the same time, a brass frame was constructed which held the two plates in rigid relation to each other. The plates were put in this frame, and when it was released by the magnet M and the catch C, Fig. 10, fell between two steel guides, shown in dotted lines. It was caught in a light-tight bag held below the slide. The guides for the plate frame were covered and made light-tight. A sliding door D, opposite the back of the camera, could be opened and ground glass inserted in place of the plate and in this manner the camera focussed.

The timing of the fall of the plates and the arrival of the ring in the field of view, so that it would be properly caught upon the plates, was accomplished in the following manner: A metal weight was so arranged that, upon releasing a catch, it would fall and make electric contact between two spring terminals in the circuit of an electric magnet, thereby releasing the plate frame; then, after a short definite time, the falling weight made contact between two other spring terminals, closing the circuit through the electromagnet gun. This timing device is shown in Fig. 11.

The relative positions of the first and second pair of contact springs could be adjusted to regulate, to a nicety, the interval

FIG. 11.



between the release of a plate and the energizing of the gun magnet. To determine the proper positions at which to set the above two contacts the following procedure was adopted: There was first suspended in the tank of water a small disk (D_1, Fig. 8) at the exact position where it was desired that the ring should be at the moment of the exposure. When a ring was projected so as to strike this disk, it would close by its impact upon the disk an electric circuit. The contact was in circuit with the primary of the transformer and also in circuit with another contact (S, Fig. 8), which normally remained closed, but which the falling of the plate frame would open at a moment when the plates were in a position to receive the image of the ring. When the trigger released the contact weight, magnet M, Figs. 8 and 10, first released the plate frame, then after an interval the gun magnet G_1 was energized, and if the ring reached the disk before the plate frame reached its exposure position, the circuit through the transformer was closed and a flash of light at the spark gaps occurred. If, however, the plate frame reached the exposure position before the ring reached the disk, the primary circuit of the transformer was open and there was no flash of light at the spark gaps. An up-and-down adjustment was made of the pair of contact springs in circuit with the gun until a flash of light of the briefest possible duration was seen. This completed the timing, which meant that the ring reached the disk at the same instant that the plate frame and plate reached the exposure position. The disk which the ring was made to strike was then removed from the tank and the circuit short-circuited at K.

By the above procedure and adjustments everything was put in readiness for exposing the plates. To decrease the danger of fogging the plates, the work was usually done at night. When all was in readiness, the main circuit switch was closed to start the spark, and the timing weight was released. This last started the plate frame on its fall and after a short interval fired the gun. The plate frame was caught in a bag and carried to the dark-room for development. There resulted, on the average, about one drop out of five which gave photographs worth preserving. There were so many things to be kept in exact adjustment at the same time that numerous failures were inevitable. The expense for plates was considerable, and the innumerable

trifles which persisted in going wrong at a critical moment were often discouraging.

After about thirteen first-class pairs of stereoscopic views had been secured and about twice this number of single views, it seemed that the research was consuming time out of proportion to the value of the results being obtained, and the writer did not feel justified in continuing the investigations further. The negatives secured, however, especially the stereoscopic ones, were sufficient to show, in a very adequate way, the precise character of the phenomena under investigation.

As the light was quite sufficient, a strong developer could be employed, and only about five minutes, as a rule, was consumed in the development of one pair of plates.

The developer employed was usually made up shortly before it was used and according to the following formula:

Water	10.7	ounces
Metol	0.5	gram
Hydroquinon	2.1	grams
Sodium sulphite	7.85	grams
Sodium carbonate	14.3	grams

This was put in a bottle with a tight glass stopper, and it was found to keep without deterioration when the bottle was kept filled. Before using it was diluted with an equal quantity of water.

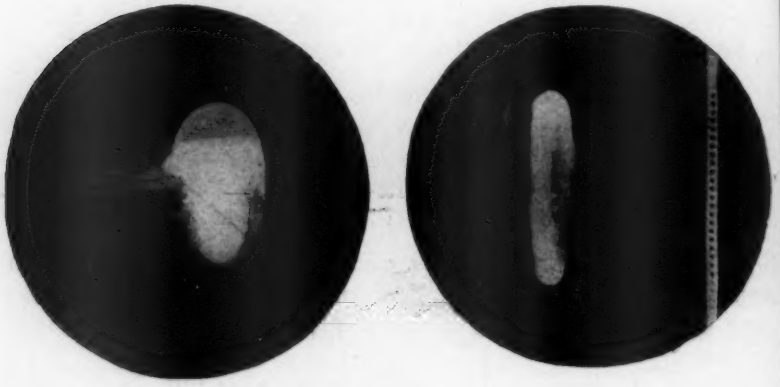
Views of rings at the moment when changing from water into oil, and at the moment of reflecting from an oil or water surface, might have been obtained by a sufficient expenditure of time and care.

From necessity the photographs were taken of the rings viewed very nearly edgewise; that is, normally to their direction of motion through the tank. It would have been interesting if views could have been secured through the lens in the end of the tank. These would have shown the rings as they appear when approaching the observer. The problem of illumination, however, was difficult, and no serious attempt was made to solve it. It was at first thought that milk-white rings might be sufficiently illuminated to be photographed by reflected light, but when this was tried with white rings of silver chloride they were found to phosphoresce for too long a time to enable in-

stantaneous photographs to be taken, even had the illumination been sufficient, which is doubtful.

View A, reproduced to be viewed in a stereoscope, is of a single ring distant a few centimeters from the gun. It has at this point a characteristic mushroom appearance and is followed by a trail of color. This ring, when photographed, was moving about one and a half meters per second. In View B is shown another ring which has also just left the gun. It probably started with a higher velocity than the ring shown in the previous view, and its mushroom head and

VIEW B. VIEW C.



trail present a smoother appearance. View C shows a ring which has gone about 30 centimeters from the gun. It started with the same appearance as the ring in View A. The trail has entirely disappeared. It also is moving more than a meter a second and is about to strike a small watch chain suspended vertically in the water. View D is of another ring taken under conditions similar to the conditions under which the ring in View C was taken. View E is of another ring, a greater distance from the gun, in which the coloring matter is less dense. If carefully observed, small dark particles may be seen to be distributed along the filamentary axis of the ring. The position of these particles does not clearly appear in a single view, but when a double view is observed in a stereoscope

which are retained in a water ring must have a density of less

VIEW A.

but when a double view is observed in a stereoscope

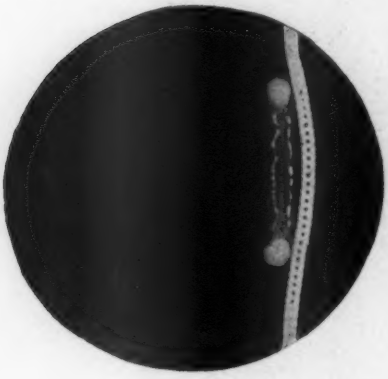
they are plainly seen to lie along the axis of the ring. In many of the views this line of dark particles is shown very clearly. While it was supposed that the coloring matter

VIEW F.

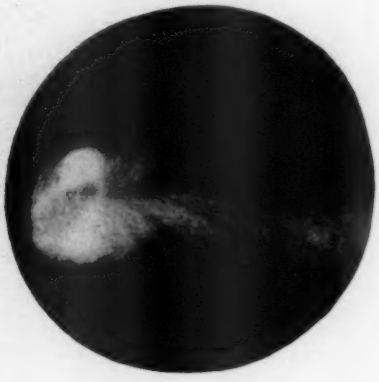
of the ring was free from suspended particles, some must have been present originally in the ring or were gathered up by it in its progress through the water. As a vortex ring throws off particles denser than the material of the ring itself, particles which are retained in a water ring must have a density of less

than water. In F we have three views, slightly smaller than the others, of the same ring, taken about 1/50 of a second apart, showing the ring just before and just after it has struck the chain. View G shows remarkably fortunate timing. The ring has moved up to, but has not actually struck, the chain. It will be noted that the chain bulges most on a line from the centre normal to the plane of the ring. The filamentary core of dark particles also shows well in this ring. The core, which seems always to be present, can generally be seen only in rings which are but slightly colored.

VIEW G.



VIEW K.



When the diaphragm of the gun is provided with two circular holes, one above the other, two rings are ejected at the same instant. The action upon each other of the two rings ejected is, perhaps, the most interesting property of these vortices. To study this action a large number of exposures of double rings were made and a few very instructive negatives secured. These views were all taken stereoptically, and to learn all they teach should be viewed in a stereoscope. Negatives were obtained of the double rings just as they were leaving the gun and also at different distances up to half a meter. In View H double rings are shown which have issued about 5 cm. from the gun. There is less coloring matter in the upper ring than in the lower, which permits the internal construction of the upper ring to be more clearly seen. Both

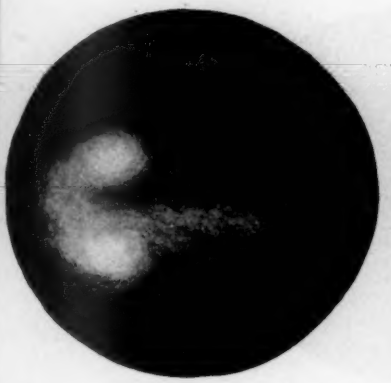
be noted that the vortex has become cleared of all surrounding

View D.

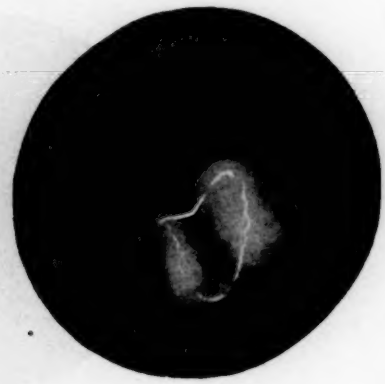
construction of the upper ring to be more clearly seen. Both

rings have the mushroom appearance characteristic of single rings just issuing from the gun. There is already an indication in this picture that the two rings are being attracted towards each other, and their planes are seen to be slightly tilted in the direction of their forward motion. The next view, I, shows two other rings a few centimeters farther from the end of the gun. The attraction towards each other and the tilting of the planes of the rings are here still more pronounced. In the following view, J, are shown two other rings a centimeter or two farther from the gun than the previous pair. Here the attraction has

VIEW L.



VIEW M.



become so great that the rings have joined. The dimly-seen cores of the separate rings, now become a single ring, show a peculiar outline, somewhat like the letter C, when viewed from a position at right angles to the forward motion of the ring. In View K the two rings have completely joined, but their trails extend back along the separate paths which they had previously followed. View L gives a slightly later stage of a double ring. In View M the vortex has become a distorted ellipse, with major axis normal to the plane of the paper. View N also shows a newly-formed double ring. View O is a ring in which the joining of the two separate rings is completed. Its phase of vibration is such that it is convex upon the side facing its direction of motion. It should be noted that the vortex has become cleared of all surrounding

coloring matter. In View P is shown another ring, also made up of two separate rings, as it appears in three successive stages separated by intervals of about 1/50 of a second. Here are plainly seen the four kinds of motion possessed by liquid vortices which have been formed from the union of two single rings. First, there is a rotation about the vortex filament; second, the forward motion of the vortex as a whole; third, a motion of oscillation of the extremities of the vertical diameter of the vortex in a vertical plane lying parallel to the direction of forward motion; and fourth, a motion of oscillation of the extremities of the

VIEW N.

horizontal diameter of the vortex in a horizontal plane parallel with the line of motion of the vortex. These four motions, except the second, are too rapid to be observed satisfactorily with the eye. But the instantaneous photographs here reproduced fairly demonstrate the nature of these motions, and the stereoscopic views especially enable their character to be accurately observed.

PHYSICAL EXPLANATIONS OF VORTEX MOTIONS.

Various physical and mathematical treatments of vortex motions that have been given by Helmholtz, Lord Kelvin, Lamb, J. J. Thomson, and others, are based, in the main, upon the assumption that the medium in which the vortices exist is a

shape, is given the simple appellation of a liquid.

View E.

so-called "perfect fluid." In Thompson and Tait's Natural Philosophy, Vol. II, § 742, the definition given for a perfect fluid is as follows: " . . . a body incapable of resisting a change of shape; and, therefore, incapable of experiencing dis-

VIEW P.

torting or tangential stress. Hence its pressure on any surface, whether of a solid or of a contiguous portion of the fluid, is at every point perpendicular to the surface." In § 320, Vol. I, the same authors say, " . . . a mass which is absolutely incompressible, and absolutely devoid of resistance to change of shape, is given the simple appellation of a liquid."

A *liquid* of this character, which is an incompressible fluid, is the ideal or perfect liquid of the mathematician. A *fluid* may be perfect and yet be a compressible fluid in which the density is a constant function of the pressure. Water does not fulfil Kelvin's definition of a perfect liquid, chiefly because of its viscosity. It is, however, nearly incompressible and relatively free from internal friction, and therefore is the most suitable of any known liquid for the experimental study of vortex motions.

Vortex motions may be studied from two diametrically opposite points of view: the mathematical and the experimental.

From the former the mathematician attempts to deduce from a few fundamental assumptions the nature of vortex motions in a so-called perfect fluid and then to predict how the viscosity of actual fluids will modify these motions.

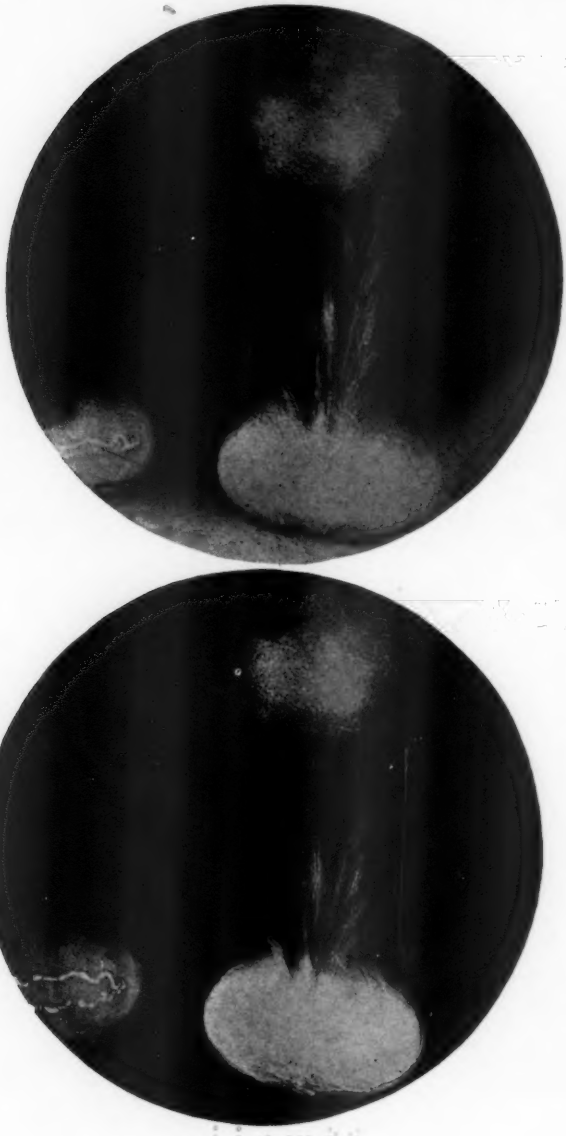
From the latter the experimentalist observes the motions in actual fluids and then reasons how they might become modified if the viscosity were to become indefinitely small. The experimental method was chosen because it is better within our capabilities and because it was believed that all actual physical problems are more likely to find their solutions when actual rather than ideal types of matter are dealt with.

The purely physical explanations, which follow, of the nature of the motions of vortices in actual liquids, may not accord in all cases with the conclusions of mathematical examinations of motions in assumed perfect fluids.

In a perfect fluid, according to the mathematicians, a vortex can never be created, or, if in existence, it cannot be destroyed. In water the vortex is easily formed and easily destroyed, while the manner of its formation is not difficult to understand.

The creation of vortices in actual fluids, their mutual action upon each other, and many peculiarities of their motions are explicable by the application of a theorem announced by Bernoulli in the 18th century. The meaning of this theorem should be clearly understood as a preliminary to any physical explanation of vortex motions.

Let the attention be fastened upon a single cubic centimeter of the liquid in the tank. Let this single cubic centimeter be h centimeters below the surface, and let the density of the liquid in the tank be d, then the mass of the single cubic centimeter will be d grams. If g is the acceleration of gravity, the weight



VIEW H.

of this cubic centimeter will be $g\ d$ dynes. Now if the imaginary cubic centimeter of liquid were lifted from its position h centimeters below the surface to the surface, the quantity of work done would equal $h\ g\ d$ ergs. Or, if we conceive the cubic centimeter of liquid replaced by a massless cube one centimeter along each edge, the work done by the rest of the liquid in raising this cube to the surface would be, as above, $h\ g\ d$ ergs. Hence the potential energy of this cubic centimeter of fluid is,

$$P_p = h\ g\ d.$$

Next conceive this same cubic centimeter of liquid to have a velocity in any direction of v centimeters per second. It would then have a kinetic energy $\frac{1}{2}\ d\ v^2$. The imaginary cubic centimeter of liquid also has additional potential energy, due to the fact that the liquid of the tank is under atmospheric pressure. This potential energy will be readily understood if we conceive a fine tube to have one end in the centre of the imaginary cube of liquid and its other end in a vacuum. The imaginary cube of liquid, if located at the surface of the liquid, would tend to flow into the vacuum with a force depending upon the pressure of the atmosphere. The potential energy due to this cause alone is simply the pressure per square centimeter upon the surface of the liquid. Call this energy p. These last statements become clear by considering that the work required to force a volume V of liquid from the vacuum back into the tank is pV. The area of the piston, multiplied by p, is the force, and the product of the force by the length of the stroke is $p\ V$, and is the work done. Hence if V is made a unit volume the work is p; that is, the potential energy due to the pressure on the liquid, per unit of volume, is simply p.

By the principle of the conservation of energy, the sum of the potential and kinetic energies of any portion of the fluid (friction neglected) must remain constant. Hence we have

$$p + g\ d\ h + \tfrac{1}{2} d\ v^2 = H, \text{ a constant.}$$

This important relation, known as Bernoulli's theorem, is to the effect that, if at any point in a fluid the velocity of the fluid increases, the pressure which the fluid will exert normally to its direction of motion will correspondingly decrease. Upon Bernoulli's principle depends the action of the aspirator, the

injector, the atomizer, the curving of golf- and base-balls, and many other phenomena familiar in aero- and hydro-dynamics. It is the sufficient principle for explaining most of the phenomena of liquid vortices.

By suitably choosing the origin of axes we may write $h=0$, when the above expression becomes

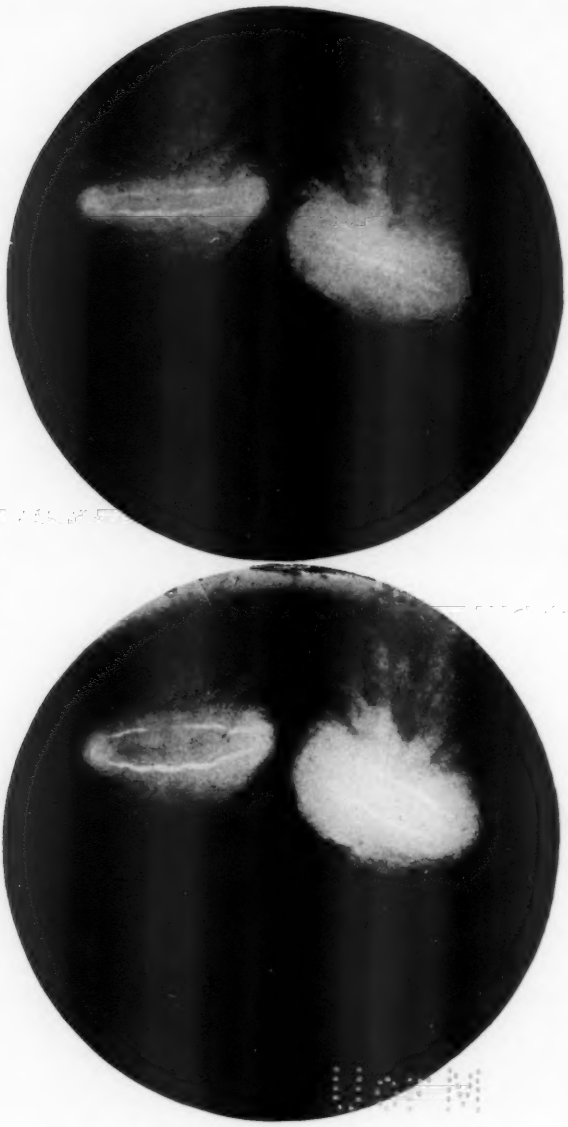
$$p+\tfrac{1}{2}d\,v^2=C, \text{ a constant.}$$

Let us consider, with this principle in mind, what happens when the diaphragm of the gun is struck a blow (Fig. 12). The diaphragm moves suddenly from p to p_1, and the stream-lines of the liquid, outside the orifice, will be somewhat as indicated in full lines. After the liquid has issued from the orifice it might have been expected to move as indicated in dotted lines. Instead, however, the stream-lines of its flow bend into spirals, as roughly indicated by the heavy lines, every particle moving towards a point where the pressure is diminishing. Now it is evident, from Bernoulli's principle, that at the edge of and just outside of the orifice the velocity of the liquid will be high and the side pressure low; hence any particle which has reached a position as *a* will be urged not from but toward the edge of the orifice, and move in a curved path approximately circular. The ring once formed continues to move forward, and the particles of liquid in it rotate rapidly about a circular centre called the vortex filament. At the beginning of motion, however, an additional body of liquid is carried along with the vortex, which is afterward left behind as a trail. The general contour of this additional body of liquid is shown in Fig. 12 by the broken heavy lines. It is due to this that a vortex possesses the peculiar mushroom appearance shown in Views A and B, taken shortly after it has left the gun.

After the ring is completely formed we have the case of particles of fluid in rapid rotation about an axial line, and the query naturally arises, why the substance of the ring is not thrown off tangentially by the action of centrifugal force.

Such, indeed, would be the case if the vortex filament did not form a closed loop. If the substance of the ring were thrown off by centrifugal force it would of necessity be replaced by other portions of the liquid. Now as the ring is closed upon itself, and as centrifugal force acts equally at every tangent to

finely suspended particles, as ground [illegible]

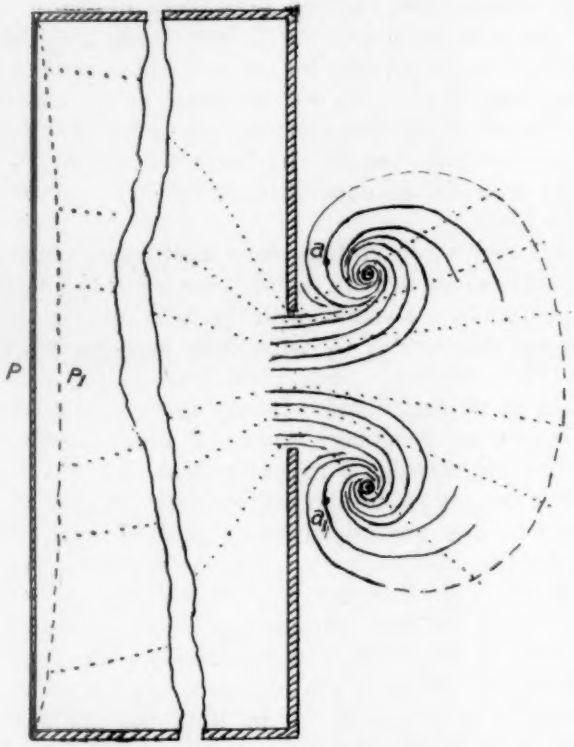


VIEW I.

...ssel, and as centrifugal force acts equally at every tangent to

a cross section, there is as much tendency for the particles of the ring to leave at one point of its surface as at another, and so even should a particle leave at a given point there would be no tendency to its replacement by a particle leaving at another point. Furthermore, as the velocity of the particles at the circumference

FIG. 12.



of the ring is high, there will be, by Bernoulli's principle, a radial pressure acting toward the filament of the vortex.

If the attempt be made to form a vortex of a more dense fluid in a less dense one, as a vortex of carbon-tetrachloride in water, a condition of instability exists, and the more dense particles of the vortex actually do fly off, impelled by centrifugal force. If a vortex ring is moving through water, filled with finely-suspended particles, as ground Indian meal, denser than

water, it will not pick up the particles. If, however, the suspended particles are less dense than water they will be swept into the vortex and carried along with it.

It is on this principle that oil rings are formed out of water rings. Assume a layer of oil on top of the water in the tank. When a water ring is made to enter the less dense oil, centrifugal force throws out the water, scattering it, and the oil is drawn in to take its place, thus forming a complete oil ring. This ring moving toward the surface of the oil will on reaching the surface be reflected and, re-entering the water, will continue to move as a stable ring of oil. As one of these oil rings is about to break up, the oil of the ring separates into small globules, which are plainly seen whirling in circular orbits about the vortex filament as an axis, in apparent contradiction to the law of centrifugal force.

The fact that liquid vortices react upon each other, and are able to cause motions in solid matter (see View G) before there is actual contact of the vortex with the solid matter, proves that the rings are surrounded by what may properly be termed a "field of fluid motion." This field consists of a system of stream-lines of moving liquid. It may be represented by drawing in the fluid an imaginary system of lines, similar to those employed for representing a magnetic field of force which surrounds a circular conductor carrying an electrical current. About the ring the fluid at any instant has a perfectly definite motion. It is this definite motion of the fluid, outside of the ring, which constitutes the field of fluid motion about the ring, which can react upon a similar field surrounding another ring. If, therefore, at every point in the fluid surrounding the ring lines be drawn in the direction of the motion of the fluid at a given instant, and if at all points in the fluid the number of lines drawn per square centimeter of area, taken normal to the direction of the lines at such points, be made equal in number to the velocity of the fluid, then this system of lines will represent, both in direction and magnitude, the instantaneous fluid motion at every point in the field.

The purpose of this article being only to record experimental results, no mathematical treatment of vortex motions will be attempted. Those interested in this phase of the subject are referred to Chapter VII of Lamb's Hydrodynamics, Third

colored liquid for colorless liquid. The portion of the final

View J.

Edition. A few physical conceptions may be given here, although these conceptions are confessedly somewhat hypothetical.

Imagine a circular vortex ring to have for an instant no forward motion. The system of lines drawn to represent the field of motion about the vortex are then assumed to be identical in form and distribution with that which would be required to represent the magnetic field of force about the ring, if it were made to carry an electric current flowing along the filamentary axis and uniformly distributed throughout the cross section of the ring. But all rings, as actually observed, have a rapid forward movement which greatly modifies the distribution of the system of stream-lines as assumed above. In actual rings some of the fluid which surrounds it is carried forward with the ring as it moves through the fluid. The general form of the body of fluid which moves with the ring is that of an oblate spheroid and gives to the ring the mushroom appearance well illustrated in View A. In View I of two rings the color of the upper ring is sufficiently pale so that the true vortex is visible within the spheroidal body of liquid which is moving with it. This spheroidal body of liquid is gradually left behind, in a liquid, like water, having viscosity, and is visible as the trail. As the ring progresses the oblate spheroid of colored liquid becomes gradually replaced by colorless liquid, and when this interchange of colorless liquid for colored is complete the oblate spheroid becomes invisible and the colored vortex only is seen. It then appears as a colored ring, shown in Views C, D, and E. These older rings, in all probability, still carry a body of liquid with them.

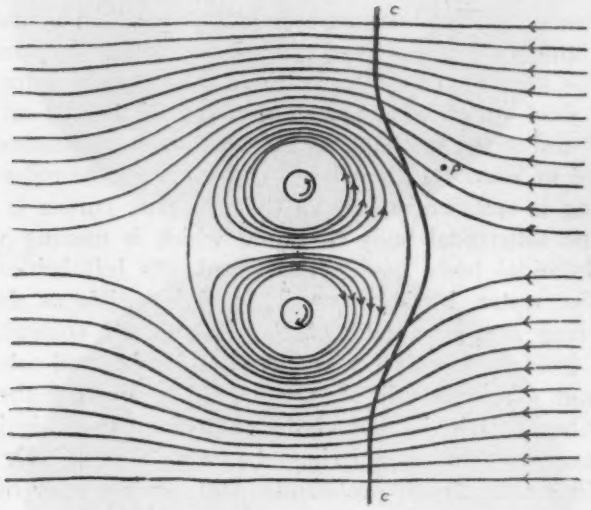
This is being drained off and replenished in exactly the same manner as appears in Views A and I.

Diagram, Fig. 13, is constructed on the assumption that the fluid has no viscosity. In it the direction of the lines represents the direction of motion of the fluid, and the density of the lines the velocity of the fluid. This velocity is reckoned in reference to the ring itself; that is, the axes of reference must be considered as having their origin located at the centre of the ring and to move with the ring. The portion of fluid within the two small circles constitutes the true vortex, which retains its color and visibility after the surrounding portion has exchanged all its colored liquid for colorless liquid. The portion of the fluid

within the elliptical line, which is a cross section of an oblate spheroid, is the portion of fluid which moves forward with the ring. If the fluid were without viscosity the ring would leave behind it no trail; that is, the same fluid contained in the oblate spheroid with which the ring started on its journey would remain with it to the end. In the actual case this body of fluid is being gradually drained off and replenished until all visibility disappears, except for the vortex itself.

Any small particle, as at *P* (Fig. 13), if more dense than

FIG. 13.



the liquid, is not caught up by the ring when the ring approaches it, but is pushed aside by the body of fluid which the ring carries with it, and receives, when the ring approaches and passes it, a small to-and-fro motion. A cord or chain suspended in the fluid, as indicated by the line *c, c,* is curved forward before it is actually reached by the ring. The View G shows this well.

With the above in mind it is not difficult, aided by the photographic views, to explain the union and subsequent double vibratory motions of the rings. For this explanation reference is made to some purely diagrammatic views given below.

In Fig. 14 *a* shows two rings a few centimeters from the gun. They are shown in side view, moving in the direction in-

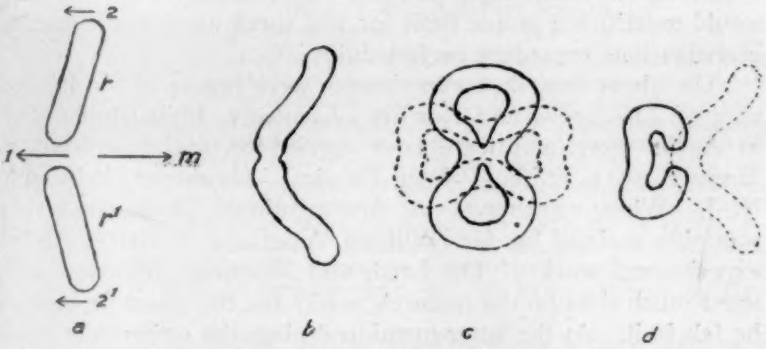
side the form shown at *a* in heavy line. This double oscillation

VIEW O.

dicated by the arrow, *m*. The velocity of the fluid *in reference to the rings* is indicated at three points by the arrows 1, 2, 2^1. Since this velocity is greater at 1 than at 2 and 2^1, the points on the circumferences of the rings which are adjacent lag behind the points which are opposite, and consequently the planes of the two rings begin to tilt forward in the manner indicated.

Furthermore, as the velocity of the fluid is greater at 1 than at other points equally distant from the filaments of the rings, there will be acting a pressure, according to Bernoulli's principle, which will tend to force together adjacent points of the circumferences of the two rings. Hence, a moment later the rings will assume a position as indicated at *b*. The rings should now

FIG. 14.



be viewed from behind, when their form will be (at a very brief instant later than shown in *b*) as indicated in full line at *c*, or in dotted line at *d*, which is a side view. The high velocity of the fluid at the point of contact has caused the two rings to unite and assume the form of a figure 8, with its upper and lower ends greatly tilted forward in the direction of motion of the now single ring.

As this distorted single ring has everywhere an equal tension along its filamentary line, it tends to assume a circular form and lie in a plane normal to the forward direction of motion. But in changing its form to assume the circular plane ring form it overshoots this equilibrium position and assumes, as seen from behind, the form shown in dotted line at *c*, and as seen from the side the form shown at *d* in heavy line. This double oscillation

about the form of equilibrium now continues, and the ring advances, its form rapidly changing in the manner which the View P beautifully reveals.

The inquiry naturally arises, Would two rings existing under similar circumstances, in a perfect fluid, or in the luminiferous ether, join together? If two vortices can unite, then would not these in turn join with others? If such be the case for perfect fluids, then it follows that a system of electrons or atoms constituted of vortices, in a perfect fluid, would not preserve their identity, but would form unions which would ultimately destroy any distinctive existence which the vortex atoms or electrons might possess.

These are questions upon which further experimentation would throw much light and the experimental facts obtained would constitute a proper basis for, and check upon, mathematical investigations regarding perfect fluids.

The above-described experiments were begun at the laboratory of The Leeds and Northrup Company, Philadelphia, Pa., in April, 1909, and were later carried on and completed in January, 1911, at the Palmer Physical Laboratory, Princeton, N. J. When working at the first-mentioned place, the writer was ably assisted by Mr. William Wrighton, in charge of the experimental work of The Leeds and Northrup Company, who spent much time on the research, solely for the scientific interest he felt in it. At the latter-mentioned place the writer was much assisted, especially in the photographic work, by Mr. Phillips Thomas. To both of these gentlemen the writer extends his grateful acknowledgments.

Subterranean Wireless Telegraphy. ANON. (*Cosmos.* No. 1369, 423.)—It is announced from Berlin that Dr. Leimbach and Dr. Loewy have transmitted subterranean wireless messages between the potash mines of the Northern Harz, over a distance of about 2½ kilometres, under the ground.

Internal Structure of Pearlitic Steel. M. OKNOF. (*Metallurgie,* viii, 138.)—By photographing the structure of samples of pearlitic steel, and then repeatedly polishing and photographing after each polishing, thus photographing successive layers, it is shown that pearlite is continuous, with the ferrite or cementite distributed through it in grains. This confirms Osmond's "cellular theory" for the structure of steel.

THE HANDLING, TRANSPORTATION AND STORAGE OF PERISHABLE FOODSTUFFS.*

A REVIEW OF THE WORK OF THE FOOD RESEARCH LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.

(Contribution from the Food Research Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.)

BY

JOSEPH SAMUEL HEPBURN, A.M., M.S.

PART III.

SELECT METHODS OF ANALYSIS.

THE ANALYSIS OF FLESH 369—THE GENERAL ANALYSIS 370—THE NITROGENOUS CONSTITUENTS OF FLESH 371—REMARKS ON THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD 373—THE DETERMINATION OF THE AMMONIACAL NITROGEN IN MEAT 374—CREATINE AND CREATININE 377—MODES OF EXPRESSING NITROGEN RESULTS 378—EXTRACTION OF THE FAT FOR ANALYSIS 378—ANALYSIS OF THE FAT 380—THE ACID VALUE, SAPONIFICATION NUMBER AND THEIR RELATED CONSTANTS 381—THE DETERMINATION OF HYDROXYL GROUPS IN FATS 384—UNSAPONIFIABLE MATTER 385—DETERMINATION OF PHOSPHORUS AND NITROGEN IN FATS 386—DETECTION OF ALDEHYDES AND ACTIVE OXYGEN 388—DETERMINATION OF THE ACID VALUE OF CRUDE FAT 389—DETECTION OF LIPASE 390—THE ANALYSIS OF MILK 390—THE ANALYSIS OF EGGS 396—BIBLIOGRAPHY 396

IN the course of the researches which have been carried out in this laboratory, old methods of analysis have been modified and new methods have been devised which are rapid yet very delicate. These methods of chemical analysis have been collected from the original sources and are embodied in the following pages:

THE ANALYSIS OF FLESH.

The chemical analysis of flesh falls into two parts, the general analysis, and the determination of the various nitrogenous constituents. The muscles[1] are separated from the bones, skin, fat and large tendons and are passed through a meat grinder several times—usually three—to obtain a fine division and thorough mixing of the flesh. The removal of the large

* Presented at the Stated Meeting of the Institute held Wednesday, May 17, 1911.

tendons of chicken muscle does not influence the analytical results, and facilitates the grinding and sampling. The samples for the various determinations should be weighed in tightly stoppered weighing bottles.

THE GENERAL ANALYSIS.

In the general analysis [2] determinations are made of the total solids and moisture, fat, ash, protein and creatine. Total solids and moisture are determined by heating 10 grams of meat, in a tared lead bottle cap of two to three inches diameter, at 100° C. in a water-jacketed oven, until the sample ceases to lose weight, and either attains a constant weight or begins to gain in weight.

The fat determination is made upon the dry residue from the total solids and moisture determination. The lead cap and its contents are cut into small pieces, placed in the thimble of a Knorr extraction apparatus, and extracted with ethyl ether, into a tared flask; an electric stove serves as the source of heat. The extraction requires 16 hours, then the ether is evaporated, and the flask and its contents are dried at 100° C. to constant weight or until a gain in weight occurs.

To determine the ash, 2 or 3 grams of meat are dried for several hours at 100° C. in a tared platinum crucible, then incinerated in a muffle until the ash is pure white. Another procedure is to dry and char the meat in the crucible, permit the latter to cool, extract the charred mass with hot water several times, and filter. The insoluble matter and filter paper are reduced to a white ash by ignition over a naked flame, with the aid of ammonium nitrate if necessary. The aqueous extract is now added to the crucible and evaporated to dryness. The crucible and its contents are then ignited in the muffle. A muffle may be prepared from a platinum dish, a piece of platinum foil and asbestos fibres. A thin layer of the fibres is placed on the bottom of the dish, which is heated with the naked gas flame. The crucible rests on the fibres, and the dish is covered with the platinum foil.

The creatine is calculated for the general analysis by multiplying the per cent. of amino acid nitrogen by the factor 3.11.

The protein is calculated by subtracting from the total per cent. of nitrogen in the flesh the per cent. of amino acid nitrogen, and multiplying the remainder by the factor 6.25.

THE NITROGENOUS CONSTITUENTS OF FLESH.

In an analysis of flesh for its nitrogenous constituents the following determinations are made:[3]

Total nitrogen of the flesh.

Total nitrogen of the aqueous extract.

Coagulable nitrogen in the aqueous extract.

Albumose nitrogen.

Amino acid nitrogen.

The total nitrogen of the flesh is determined directly upon the flesh; for the determination of the other constituents, an aqueous extract is prepared. Peptone nitrogen and nitrogen insoluble in water are determined by difference. Frequently direct determinations are also made of the ammoniacal nitrogen, creatine and creatinine.

The total nitrogen of the flesh is determined by the Kjeldahl method upon a two-gram sample of the ground muscle.

For the preparation of the aqueous extract of the flesh, 44 grams of the ground muscle are shaken gently with 300 c.c. of water in a glass bottle, upon a shaking machine, for 15 minutes. If the shaking be too violent an emulsion is formed which cannot be filtered even after the use of a centrifuge. The bottle is then transferred to an electric centrifuge and rotated for 20 minutes to settle the insoluble matter. The solution is filtered through paper, using folded filters. The residue is extracted as before, and extraction is continued until the filtrate no longer responds to the biuret reaction. Thymol should be used during the extraction to inhibit the action of both organized and unorganized ferments. The filtrate is neutralized with N/10 sodium hydroxide solution, using litmus as indicator, and is diluted to 2000 c.c.

To determine the total nitrogen of the aqueous extract, 100 c.c. are placed in a Kjeldahl flask of 500 c.c. capacity, concentrated sulphuric acid is added, and a gentle heat is applied until the water has evaporated; the digestion is then carried out in the usual way.

The nitrogen coagulable by heat, the albumose nitrogen and the amino acid nitrogen are determined on 500 c.c. of the aqueous extract. The coagulation is carried out on an electric stove; if the beaker be placed upon a piece of asbestos board and be covered with a watch glass, coagulation occurs as the solution

concentrates. When the volume of the solution has reached 100 c.c., the coagulum is compact, does not adhere to the beaker and may be filtered and washed with ease. Should coagulation be imperfect, the addition of a few drops of very dilute acetic acid will obviate the difficulty. The coagulum is filtered and washed with boiling water until the washings no longer respond to the biuret reaction. The filter and precipitate are transferred to a Kjeldahl flask for digestion.

The filtrate and washings are concentrated to 100 c.c. on the electric stove, then divided into two portions of 50 c.c. each; one portion serves for the albumose determination, the other for the determination of amino acids.

The portion for the determination of albumose nitrogen is evaporated to 30 c.c. in a beaker of 150 c.c. capacity on the electric stove; the beaker is removed from the stove, 1 c.c. of 50 per cent. sulphuric acid is added at once, followed by 40 grams of crystalline zinc sulphate. The solution must be well stirred so that the zinc sulphate will dissolve completely; it is again heated, then allowed to cool and stand for 12 hours to permit separation of the precipitated albumoses. If no crystals of zinc sulphate have separated, more of that salt must be added, the solution again be heated, then permitted to cool in order to insure saturation with the salt at ordinary temperature. The albumoses are collected on a filter in the cold and are washed with a cold, saturated solution of zinc sulphate, faintly acid with sulphuric acid. Filter and precipitate are then subjected to the Kjeldahl method for the determination of nitrogen. This method for the separation and determination of albumoses is based on that of Bömer.[4]

The 50 c.c. portion for the determination of amino acids is transferred to a graduated flask of 100 c.c. capacity, 15 grams of sodium chloride are added, and the flask is placed in an ice box for an hour. Then 30 c.c. of an ice-cold 24 per cent. solution of tannin are added, the flask is filled to the mark with ice-cold distilled water, and the contents are well mixed. The flask and its contents remain in the ice box for 24 hours, then the precipitate is removed by filtration. Unless flask and funnel are kept cold during this operation, re-solution of the precipitate is apt to occur. The nitrogen is determined in 50 c.c. of the filtrate, hence the calculation is made on a sample of 2.75 grams. A blank determina-

tion must be made with each experiment, for tannin always contains nitrogen; allowance for the nitrogen content of the blank must be made in the calculation of the amino acid nitrogen. This determination also includes the nitrogen of ammoniacal compounds, *i.e.*, ammonia and amines, if such be present. This method is that of Bigelow and Cook.[5]

From the preceding paragraphs, it follows that the volume of aqueous extract of the flesh used for the determination of the total nitrogen of that extract represents a sample of 2.2 grams of the meat, while the volume used for the determination of the soluble nitrogen coagulable by heat corresponds to a sample of 11 grams of the meat. In like manner, the volume of the filtrate from the coagulum used for the determination of albumoses represents a sample of 5.5 grams of the meat, while the volume of the filtrate from the tannin precipitate used in the determination of amino acid nitrogen corresponds to a sample of 2.75 grams of the meat.

The peptone nitrogen is determined by difference by subtracting from the per cent. of total nitrogen of the aqueous extract the sum of the per cents of coagulable nitrogen, albumose nitrogen and amino acid nitrogen.

The nitrogen insoluble in water is determined by difference by subtracting from the per cent. of total nitrogen in the flesh the per cent. of total nitrogen soluble in water.

Pictures of the shaking machine, centrifuge, and still used in this work were published in Part I of this paper, JOURNAL OF THE FRANKLIN INSTITUTE, 1911, CLXXI, 588–590.

REMARKS ON THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

The various modifications of the Kjeldahl method have been discussed in a recent paper in this journal.[6] The Gunning modification has been found to be an excellent method for the determination of the nitrogen content of substances of animal origin, and is used in this laboratory several thousand times each year. Kjeldahl flasks of 500 c.c. capacity are used for both digestion and distillation. The sample is digested for 4 hours with 25 c.c. of concentrated sulphuric acid, 10 grams of potassium sulphate, and a small fragment of crystalline cupric sulphate not exceeding 0.2 gram in weight. The digested material is dissolved in

250 c.c. of distilled water; an excess of concentrated sodium hydroxide solution (as a rule 100 c.c.) is poured in so that it sinks beneath the solution, a small quantity of granulated zinc is added, the flask is connected with a safety splash trap or distilling head and a block tin condenser, and the contents are well mixed by shaking. To avoid action of the standard acid on the tin and consequent vitiation of the results, a glass tube is attached to the lower end of the block tin condenser, and dips into the N/10 sulphuric acid which absorbs the ammonia. The distillation is carried out in the usual way and the excess of acid is titrated with N/10 sodium hydroxide, using Congo red as the indicator. A blank determination should be made upon the reagents which usually contain slight but appreciable quantities of nitrogen.

In determining the amino acid nitrogen, 30 c.c. of concentrated sulphuric acid are used; no potassium sulphate is added, for the sodium chloride gives rise to an equivalent quantity of sodium sulphate; until the liberated hydrochloric acid has escaped, a gentle heat must be applied; then the heat should be increased and digestion continued for 5 hours.

Fats and substances rich in fat like egg yolk require a larger quantity of sulphuric acid and a longer period of digestion than do most substances of animal origin. In the digestion of fats, it is prudent to use 800 c.c. Kjeldahl flasks; the digested material may be transferred to a 500 c.c. flask for distillation.

THE DETERMINATION OF THE AMMONIACAL NITROGEN IN MEAT.

Usually the determination is made by subjecting the meat to distillation in the presence of magnesium oxide, and titrating the ammoniacal compounds in the distillate.

Thus Richardson and Scherubel [7] give two methods for the determination of "ammoniacal nitrogen." In their "first method" they distil 25 grams of meat, 10 grams of magnesium oxide and 450 c.c. of water, contained in a litre flask, so that 200 c.c. of distillate collect in from 50 to 60 minutes. The distillate is received in a flask containing N/10 acid, and the excess of acid is determined at the end of the distillation. "Comparable results are obtained in one distillation, but if sufficient water is added to make up the original volume and distillation repeated, more ammonia distils over. After four or five distillations a practical limit is usually reached." In their "second method,"

they direct that 100 grams of the meat be extracted three times with 150 c.c. of 60 per cent. alcohol; each extract is filtered through cheese-cloth, which is wrung tightly. The three portions of extract are combined, 10 grams of freshly calcined magnesium oxide are added, and the solution is subjected to distillation so that exactly 200 c.c. of distillate collect in 30 minutes; N/10 acid is used as in the preceding method; a blank determination must also be carried out. "Results by this method are usually about one-third to one-half those obtained by the first method."

Richardson and Scherubel state: "We attach considerable importance to the ammoniacal nitrogen determination by both the methods which we have used, although these methods are comparative and not absolute."

The chief fault in the method of Richardson and Scherubel lies in the fact that, although a large portion of the ammoniacal compounds distil during the first period, evolution of these compounds never ceases; thus in a study of hashed fresh meat, these investigators still obtained ammoniacal nitrogen during the tenth period of distillation by their "first method" and during the fourth period of distillation by their "second method."

Pennington and Greenlee[8] attempted to determine the ammoniacal nitrogen in chicken meat according to the "first method" of Richardson and Scherubel; however, the results were far from satisfactory, for ammoniacal nitrogen was obtained in comparatively large quantities during the fourth, fifth and sixth periods of distillation. Thus a fowl kept at 32° F. for 24 hours after slaughter, then analyzed, yielded 0.016 per cent. ammoniacal nitrogen during the fourth period of distillation, and a fowl, which was kept for 48 hours after slaughter at 32° F., then for 72 hours in a cool room, upon analysis yielded 0.016 per cent. ammoniacal nitrogen during the sixth period of distillation. Evidently boiling the flesh with even such a mild alkali as magnesium oxide gives rise to proteolysis and gradual formation of amines or similar nitrogenous compounds, with consequent vitiation of the analytical results.

Therefore the use of magnesium oxide and heat was abandoned, and the method of Folin[9] for the determination of ammonia in the urine and other animal fluids was applied in modified form to flesh analysis. The method depends upon the

complete removal of the ammoniacal compounds from the meat by a strong current of air in the cold, in the presence of a mild alkali. The air current is created by a vacuum pump driven by an electric motor. The air passes through sulphuric acid in a wash bottle, which is provided with a safety splash trap such as is used in Kjeldahl distillations, then through a flask which functions as an air trap. "It then passes through a litre flask in which 25 grams of finely-ground meat are suspended in 250 c.c. of water, with 5 grams of magnesium oxide. Between this flask and the 0.1N sulphuric acid absorption bottle is an empty 250 c.c. flask to catch any mechanical spattering or frothing; and beyond the acid bottle a 100 c.c. flask is placed to catch any particles of the acid that may pass into the exit tube. The flasks are set up in batteries of four, using one brass or glass four-way tube to connect with the air pump, and another of similar form leading to the air wash bottle." At the end of the determination the 100 c.c. flask and the tubes connecting it to the absorption flask are washed out into the latter, and the excess of acid is titrated, using Congo red as an indicator. The usual period of aspiration is 5 hours; 2 grams of sodium carbonate may be substituted for the magnesium oxide.

"The addition of about 25 c.c. of alcohol largely prevents the foaming of the protein, which may happen during the latter part of the aspiration period. When once started but little attention is required except an occasional shaking of the flasks. One gram of sodium fluoride, and a temperature of 10–15°, has been found a satisfactory method of preserving unchanged the suspension of meat in water for a period of 24 hours—a fact which is of considerable importance, if many samples are received at one time.

"Like the evolution by distillation with magnesium oxide, the preponderance of ammonia is given off during the first hour, but, unlike that procedure, there is a steady decrease until the zero point is reached."

In certain experiments, the absorption apparatus was changed at intervals; it was thus determined that in from 4 to 6 hours the air current gave rise to a quantitative separation of ammoniacal nitrogen from the flesh of chickens, of which one had been held at 32° F. for 24 hours after killing, another had been kept in a cool room for 6 days, and still another had been kept hard

frozen for 2 years. During further aspiration, absolutely no ammoniacal nitrogen was evolved by these samples.

A picture of the apparatus of Pennington and Greenlee appears in Part I of this paper, JOURNAL OF THE FRANKLIN INSTITUTE, 1911, CLXXI, 592.

CREATINE AND CREATININE.

Creatine is methyl guanidine acetic acid, while creatinine is the corresponding anhydride formed by elimination of one molecule of water from one molecule of creatine.

These compounds are determined colorimetrically. According to Folin,[10] " 10 milligrams of creatinine dissolved in 10 c.c. of water give the maximum red color five to ten minutes after addition of 15 c.c. of 1.2 per cent. picric acid solution and 4 to 8 c.c. of 10 per cent. sodium hydroxide. The solution obtained in this way diluted to 500 c.c. gives a liquid of which 8.1 mm. in transmitted light have exactly the same color as 8 mm. of N/2 potassium bichromate solution." The half normal potassium bichromate solution contains 24.54 grams of that salt in one litre of solution. Creatine, on the other hand, does not react with alkaline picric acid solution to form a red color.

In flesh analysis the creatine and creatinine are usually determined together, the creatine being converted into its anhydride during the course of the analysis. Cook[11] has recently studied the factors which influence the creatinine determination. He directs that 25 grams of finely ground meat be shaken with 200 c.c. of water for 1 hour, the extract is decanted and the insoluble residue is shaken for an hour with 200 c.c. of water, then the extract is decanted and the insoluble residue is washed with 50 c.c. of water. In the preparation of this aqueous extract, the shaking machine and the centrifuge are used. The combined extracts and washings are evaporated to a volume of 75 to 100 c.c., then filtered. The filter is washed, and the filtrate and washings are evaporated to a volume of 50 c.c. in a small Erlenmeyer flask, 25 c.c. of normal hydrochloric acid are added, and the flask and its contents are heated in an autoclave for 15 minutes at 117° C., in order to dehydrate the creatine. The solution, which now contains the preformed or original creatinine of the meat plus the creatinine derived from the creatine of the

meat by dehydration, is neutralized and evaporated to 50 c.c. Ten c.c. of this solution, equivalent to 5 grams of meat, are mixed with 25 c.c. of 1.2 per cent. picric acid solution and 10 c.c. of 10 per cent. sodium hydroxide solution, let stand for 5 minutes to permit the color to develop, then diluted to 500 c.c., and immediately compared in the Duboscq colorimeter with N/2 potassium bichromate solution, in which the prism is set at 8 mm. From the colorimeter readings, the per cent. of creatinine is calculated by simple proportion.

MODES OF EXPRESSING NITROGEN RESULTS.

Direct analysis gives the percentage of the different nitrogenous constituents present in the sample as prepared for analysis, and makes no allowance for the varying quantities of fat, ash and water which are present in the muscle. In order to compare several samples with respect to their nitrogenous constituents, it becomes necessary to recalculate these results in such a manner that the disturbing factors are eliminated. This object may be attained in two ways, by recalculation to the fat-ash-water-free basis, or by expressing the various forms of nitrogen as per cents of the total nitrogen of the flesh. The results on the fat-ash-water-free basis are of value chiefly in comparing the total amount of nitrogen in the muscle, while the results as per cents of the total nitrogen offer an excellent method for the comparison of the various forms of nitrogen, such as total nitrogen of the extract, albumose nitrogen, etc.

The recalculation to the fat-ash-water-free basis is made by multiplying each form of nitrogen, as determined by analysis, by a factor, which is obtained as follows:

a = Total Solids
b = Fat
c = Ash
x = Factor

$$x = \frac{100}{a-(b+c)}$$

EXTRACTION OF THE FAT FOR ANALYSIS.

In the preparation of chicken fat for analysis,[12] the crude abdominal and subcutaneous fat and the skin are ground in a

meat chopper, placed in a thimble, and extracted for two days in a Soxhlet extractor with redistilled petroleum ether of boiling point 40–60° C. The solution of fat is then filtered to remove any solid particles which may have been carried over mechanically from the thimble, the solvent is evaporated on the water bath, and the fat is placed in a vacuum desiccator over calcium chloride to remove the last traces of petroleum ether. Fats should never be placed in a vacuum over concentrated sulphuric acid, for the vapors of the acid will exert a harmful influence on the fat; thus the fat of a perfectly fresh chicken, treated in this way, had the enormously high acid value 44.9. Jannasch [13] states that traces of the vapor of sulphuric anhydride and sulphurous acid may be present in the atmosphere of an ordinary desiccator containing concentrated sulphuric acid. Of course, in a vacuum the quantity of these vapors would be much greater.

The extraction of fat from egg yolk [14] is a more difficult task. Since the yolk contains about 50 per cent. of water, it is necessary to dehydrate the yolk before extracting the fat. The dehydration is carried out by means of alcohol. The yolks of a number of eggs are mixed by stirring, then slowly poured, with constant stirring, into several times their volume of alcohol. The coagulated material is collected upon a filter, and extracted for two days with alcohol in a Soxhlet extractor. The filtrate and extract are combined and distilled on a water bath in vacuum. The residue from the distillation is taken up in redistilled petroleum ether, which is then used for the fat extraction. The coagulated yolk, after having been extracted with alcohol, is ground in a meat chopper, and placed over calcium chloride in a vacuum desiccator in order to remove the last traces of alcohol. The ground material is then extracted with redistilled petroleum ether in the usual way, in a Soxhlet extractor.

Butter fat may be extracted from cream in the same manner as fat is extracted from egg yolk.

If ethyl ether be substituted for petroleum ether, the fat constants will be influenced in value by the change of solvent. This fact is made clear by the following experiments in which the crude abdominal fat of chickens was divided into two portions, of which the one was extracted with ethyl ether, the other with redistilled petroleum ether.

Sample Number	352		353	
Solvent	Ethyl Ether	Petroleum Ether	Ethyl Ether	Petroleum Ether
Iodine Number.	75.4	75.0	70.7	70.0
Acid Value	1.7	1.8	1.6	1.5
Saponification Number	197.2	194.4	195.2	188.2
Ester Value	195.5	192.6	193.6	186.7
Hehner Number	96.41	94.27	96.51	93.49

ANALYSIS OF THE FAT.

In the course of the analysis of a fat in this laboratory, any or all of the following determinations may be made:

Specific Gravity.
Index of Refraction.
Viscosity.
Iodine Number.
Reichert-Meissl Number.
Acid Value.
Saponification Number.
Ester Value.
Soluble Acids.
Hehner Number.
Acetyl Value.
Acetyl Saponification Number.
Lactones.
Unsaponifiable Matter.
Phosphorus Content.
Nitrogen Content.
Aldehydes.
Active Oxygen.

Certain of these determinations are so well known that they need not be described in detail. The specific gravity is usually obtained by means of a pyknometer. The index of refraction is determined with a water-jacketed Abbé refractometer,[15] the viscosity by means of a torsion viscosimeter.

The iodine number is determined by the method of Hanus [16] as modified by the Association of Official Agricultural Chemists.[17] The determination of the Reichert-Meissl number is carried out according to the method of Leffmann and Beam.[18]

THE ACID VALUE, SAPONIFICATION NUMBER AND THEIR RELATED CONSTANTS.

The most convenient and accurate method for the determination of the acid value is based on the use of alcohol [19] as a solvent. From 5 to 20 grams of fat are weighed out in a tared flask, 50 c.c. of previously neutralized 95 per cent. alcohol are added and the flask is heated on an electric stove until the alcohol boils vigorously; the free fatty acids pass into solution in the boiling alcohol and are immediately titrated with N/10 sodium hydroxide, using phenolphthalein as an indicator.

By another method,[12] the fat is weighed out in a tared flask, 100 c.c. of a 15 per cent. solution of sodium chloride are added, the flask is immersed in hot water until the fat is liquefied, then the free acids are titrated with N/10 sodium hydroxide, phenolphthalein serving as the indicator; the flask must be shaken frequently and vigorously until a distinct pink color appears. If the fat has a high acidity, the sodium chloride salts out the soap formed in the titration, and this hard soap encloses the fat and fatty acids and thus interferes with the titration; the difficulty may be overcome by use of a 15 per cent. solution of potassium chloride, for soft soaps do not exert such a harmful influence on the titration. This method can be used only with oils and fats of low melting point. Fats which have a fairly high melting point, *e.g.*, egg fat, solidify during the titration, enclose free fatty acid and give too low a result. This is shown by the following determination of the acid value of the same egg fat by the two methods:

Method	Acid Value
By potassium chloride	2.7
By ethyl alcohol	5.8

The alcohol method, on the whole, is far superior to the alkali chloride methods.

The saponification number is determined by saponifying 5 grams of fat in a tared flask by means of 50 c.c. of a 4 per cent. solution of potassium hydroxide in redistilled, aldehyde-free alcohol.[20] The saponification is carried out on an electric stove. A blank determination is carried out, and, after the flasks and their contents have cooled, both determination proper and blank

are titrated with N/2 hydrochloric acid, using phenolphthalein as indicator. The difference between the number of c.c. of standard acid required to neutralize the blank and to neutralize the determination proper are a measure of the quantity of potassium hydroxide required to saponify the sample of fat, hence the saponification number may then be calculated.

In determining the saponification number of dark fats the end point of the final titration, although definite, is at times quite difficult to recognize. In order to overcome this difficulty, the suggestion [21] has been made that for phenolphthalein be substituted the indicator known as alkali blue 6B, which is blue with acids and red with alkalies and is sensitive to fatty acids. Two c.c. of a two per cent. solution of the indicator in alcohol are used in each titration. In titrating egg fat saponification numbers with alkali blue 6B, the writer has found the end point to be modified to green, due doubtless to the chromogenic matters of the fat; the end point, however, is quite definite.

Stiepel [22] has devised the following procedure for determining the saponification number of dark fats and oils. Five grams of fat are saponified in the usual way with alcoholic potash, barium chloride is added—20 c.c. of a normal solution should suffice—then 300 to 400 c.c. of recently boiled water. The flask is heated for 30 minutes beneath a reflux condenser to exclude carbon dioxide; the barium soaps are precipitated and carry down with them all the coloring matters. The excess of alkali may then be titrated with N/2 hydrochloric acid in the supernatant liquid; or if the precipitate make difficult the recognition of the end point, it may be removed by filtration and the titration be made on an aliquot portion of the filtrate. Phenolphthalein is used as an indicator.

These three methods give almost the same value for the saponification number, as is shown by the following results which were obtained upon the same egg fat:

Method.	Saponification Number.
Titration with phenolphthalein	190.1
Titration with alkali blue 6B	188.4
Barium chloride precipitation	187.5

The ester value is usually determined by subtracting the acid value from the saponification number. However, at times the small quantity of material at the disposal of the analyst compels the direct determination of the acid value and ester value upon the same sample, and calculation of the saponification number by addition of the two constants directly determined. The free acids are titrated by the alcohol method and the acid value is calculated; then alcoholic potash is added and the neutral esters are saponified, a blank determination is carried out, both determination proper and blank are titrated, and the ester value is calculated. By addition of acid value and ester value, the saponification number is obtained.

From the saponification number may be calculated the mean molecular weight of a fat, and the mean number of carbon atoms in the fatty acid molecule. The latter calculation is based on the assumption that the fat is a neutral, saturated triglyceride; the presence of free fatty acid, of unsaturated acids and of unsaponifiable matter is disregarded; however, the presence of these compounds would tend to give a higher value for the number of carbon atoms in the fatty acid molecule.

Let x equal the mean molecular weight of the fat, and y the saponification number.

$$\begin{array}{rcl} \text{Fat} : 3\ \text{KOH} & = & \text{Weight fat} : \text{Weight KOH} \\ x\ : 3\ (56.11) & = & 1\ \ : 0.001y \end{array}$$

$$x = \frac{168.33}{0.001y}$$

The triglyceride of a saturated fatty acid has the general formula $(C_nH_{2n-1}O_2)_3C_3H_5$; equating this formula to the mean molecular weight and substituting for carbon, hydrogen and oxygen their respective atomic weights, it follows that

$$3(12n + 2n - 1 + 32) + 36 + 5 = X.$$

Solving for n, the number of carbon atoms in the fatty acid molecule,

$$n = \frac{x - 134}{42}$$

The determination of the soluble acids and of the insoluble acids (Hehner number) is usually combined with that of the

saponification number,[20] according to the official method of the Association of Official Agricultural Chemists, to which reference must be made for the details of the procedure.

In determining the acid value and saponification number, Erlenmeyer flasks of 300 c.c. capacity are most convenient.

THE DETERMINATION OF HYDROXYL GROUPS IN FATS.

From a study of certain constants of a pure fat or oil and of the same fat after acetylation, the presence of hydroxyl groups may be detected. These hydroxyl groups are usually present as hydroxy acids, *e.g.*, in castor oil, but may also occur as free alcohol groups, either in mono- and diglycerides or in the aromatic alcohols cholesterol and phytosterol. The saponification number of the acetylated fat is termed the acetyl saponification number. If the acetyl saponification number be higher than the saponification number proper, then hydroxyl groups are present in the fat, and have been converted into acetyl groups during the process of acetylation.

The acetyl number is a measure of the hydroxyl groups. The determination of this constant may be made with accuracy in a short time by the filtration method of Lewkowitsch.[23] Five grams of the acetylated fat are saponified with an accurately measured quantity of standardized alcoholic potash. The alcohol is evaporated, the soap is dissolved in water, a known excess of standardized sulphuric acid is added, the flask is heated gently beneath a reflux condenser until the insoluble acids form an oily layer, they are then removed by filtration and washed until the washings are no longer acid. The filtrate and washings are combined and titrated with N/10 sodium hydroxide, using phenolphthalein as indicator. The result is expressed as acetyl number, *i.e.*, "the number of milligrams of caustic potash (KOH) required for the neutralization of the acetic acid obtained on saponifying one gram of the acetylated fat or wax." After allowing for the known excess of mineral acid, the number of cubic centimeters of N/10 sodium hydroxide is multiplied by 5.611 and divided by the weight of the acetylated fat; the result is the acetyl value. Lewkowitsch[24] terms the value thus obtained the "apparent acetyl value;" he determines in like manner the quantity of potassium hydroxide required to saturate the volatile

acids of the original fat, subtracts this from the apparent value and thus obtains the "true acetyl value" which is the correct measure of the hydroxyl groups.

If the insoluble fatty acids of a fat or oil be isolated and their saponification number and acid value be determined, at times the saponification number will be found to be higher than the acid value, although one would expect the two constants to be the same. This difference between the two constants is due to the presence of lactones in the free acids [25] and therefore indicates the presence of hydroxy acids in the fat. Lactones are not neutralized during the titration in the determination of the acid value; but the lactonic ring is opened by the boiling alcoholic potash during the determination of the saponification number, and the hydroxy acids thus formed are neutralized by the alkali, and thus cause the saponification number to be higher than the acid value.

The following data obtained by the analysis of fat from fresh chickens, laboratory number 340, are concrete examples of the facts just enumerated. The presence of hydroxyl groups —hydroxy acids—is shown (1) by the fact that the acetyl saponification number is higher than the saponification number of the fat, (2) by the acetyl value, and (3) by the saponification number of the insoluble fatty acids, which is higher than their acid value.

Saponification number of the fat	196.2
Acetyl saponification number of the fat	200.6
Acetyl value of the fat	7.4
Acid value of the insoluble acids	187.2
Saponification number of the insoluble acids	198.9

UNSAPONIFIABLE MATTER.

The following method for the determination of the unsaponifiable matter in a fat has proved satisfactory. Ten grams of fat are saponified by boiling with alcoholic potash beneath a reflux condenser. The resulting solution is transferred to a casserole, while hot; five grams of sodium bicarbonate and about one hundred grams of sand (previously ignited and allowed to cool) are added, the solution is evaporated to dryness on the water bath, then heated for several hours in the water-oven to insure

complete dryness. The resulting mass is ground in a mortar, then placed in the thimble of a Soxhlet extractor and extracted with ethyl ether into a tared flask. The extraction requires two days. The mortar and casserole are washed with ethyl ether, which then is filtered and added to the extract in the tared flask. The ether is evaporated and the flask and its contents are dried in the water-oven until the weight either becomes constant or increases. The quantity of unsaponifiable matter is then calculated. The ether must be redistilled over sodium.

If it be desired to investigate the nature of the unsaponifiable matter, a larger sample of fat should be used. To separate the cholesterol from the unsaponifiable matter of egg fat, clarification by means of purified animal charcoal, and recrystallization from methyl alcohol according to Cappenberg [26] form an excellent procedure. Cappenberg dissolves the material in hot methyl alcohol, filters while hot, adds 20 per cent. of water, concentrates until crystallization begins, then cools to 0° C., whereupon all the cholesterol crystallizes out. The precipitate is collected on a filter and washed first with 50 per cent. methyl alcohol, then with hot water. Cholesterol may be identified by its crystalline form, or, according to Bömer,[27] by the melting point of its acetate.

DETERMINATION OF PHOSPHORUS AND NITROGEN IN FATS.

In order to determine the phosphorus content of a fat, it is first necessary to destroy the organic matter; this may be done by digestion with sulphuric acid or by combustion with sodium peroxide. If the former procedure [28] be chosen, the weighed sample of fat is digested in a Kjeldahl flask with concentrated sulphuric acid and potassium sulphate until the contents of the flask are perfectly clear and colorless. Addition of a small fragment of cupric sulphate will hasten the digestion. The digested material is dissolved in water, transferred to a beaker, made alkaline with ammonia, then acid with nitric acid; fifteen grams of ammonium nitrate are added to the hot solution, followed by 50 c.c. of the official ammonium molybdate solution for each decigram of phosphoric oxide which may be present. The beaker and its contents are permitted to stand over night in a warm room to insure complete precipitation of the ammonium phosphomolybdate. The precipitate is collected upon a filter, washed

with 10 per cent. ammonium nitrate solution, then dissolved off the filter by means of ammonium hydroxide and hot water; the volume of the solution thus obtained should not exceed 100 c.c. The solution is almost neutralized with hydrochloric acid and permitted to cool to room temperature. Fifteen c.c. of official magnesia mixture, for each decigram of phosphoric oxide which may be present, are added drop by drop, followed after a period of fifteen minutes by 12 c.c. of concentrated ammonia. The precipitate of ammonium magnesium phosphate is permitted to stand over night, then collected on a tared Gooch crucible, washed with 2.5 per cent. ammonia, ignited in a muffle to magnesium pyrophosphate and weighed.

A modification of the sodium peroxide combustion method of LeClerc and Dubois [29] may be used to determine the phosphorus content of a fat. The weighed sample of fat is first saponified in the nickel crucible by heating with 5 grams of anhydrous sodium carbonate and sufficient water. The crucible is then allowed to cool, and the combustion is carried out as directed by Dubois.[30] The fused mass is dissolved in hot water, and the solution is acidulated with nitric acid. The phosphoric acid is precipitated as ammonium phosphomolybdate and finally weighed as magnesium pyrophosphate.

Of the two methods, digestion with sulphuric acid permits the use of a larger sample, and also requires less attention than the combustion with sodium peroxide.

The writer prefers the gravimetric method for the determination of sulphuric acid; however, should it be desired to use the volumetric method [31] (solution of the ammonium phosphomolybdate in a known volume of standard fixed alkali hydroxide, and titration of the excess of alkali with standard mineral acid, using phenolphthalein as an indicator) in connection with the sodium peroxide combustion, it is essential that the directions for precipitation, according to the volumetric method, be followed in every detail, on account of the influence of the conditions of formation upon the constitution of ammonium phosphomolybdate. Thus Gillan,[32] who has recently made a study of this complex salt, reaches the conclusion " that the conditions of formation largely determine the constitution of the salt, and it is evident that to get a constant ratio for the acid content it is necessary to work under very definite conditions as to quantity of material present, and as

to the dilution of the solution in which the complex salt is formed." Wherry [33] has suggested that the complex inorganic acids and their salts are not true chemical compounds, but partake rather of the nature of the so-called "absorption compounds."

The determination of the nitrogen content of fat has already been described in the chapter upon the determination of nitrogen by the Kjeldahl method.

DETECTION OF ALDEHYDES AND ACTIVE OXYGEN.

The literature upon the occurrence of aldehydes and active oxygen in fats and oils, which have been exposed to the action of the forces of Nature, has been reviewed in a previous contribution from this laboratory.[34] It will therefore suffice to state that the following methods have been tried and found to be of value in detecting these compounds in such fats.

Aldehydes frequently occur in both crude and extracted fats which have been exposed to the action of the air for some time. They may be detected by means of fuchsin sulphurous acid [35] which is prepared by mixing the following reagents in the given order:

30 c.c. of an 0.1 per cent. solution of fuchsin.
20 c.c. of sodium bisulphite solution of 34° Baumé.
200 c.c. of water.
3 c.c. of sulphuric acid of 66° Baumé.

Ten c.c. of the reagent and 2 c.c. of the molten extracted fat are mixed and well shaken; the maximum color develops within half an hour. After the fat and the aqueous layer have separated on standing, the violet color appears in the fat. Occasionally the aqueous layer also assumes a violet tint.

The test may also be applied to finely divided crude fat. Several grams of the fat are placed in a test tube, which is immersed in warm water to render the fat, then is permitted to cool to room temperature. Ten c.c. of the reagent are added and the experiment is carried out as with extracted fats.

Active oxygen may be detected in fats by Legler's test or by Walker's test. Legler [36] recommends that 10 c.c. of water be warmed in a test tube, an equal volume of the molten fat be added, then several drops of a solution of neutral lead acetate and of ammonia water. The mixture is shaken vigorously. If

active oxygen be present, the mixture is colored from a pale yellow to a deep orange-brown, due to the formation of hydrated lead peroxide; the intensity of the color depends on the quantity of active oxygen present in the fat.

Walker's test [37] for active oxygen is based upon the liberation of iodine from potassium iodide by active oxygen in the presence of acetic acid. This test exists in two modifications. Potassium iodide-starch paper is saturated with the fat, a drop of 10 per cent. acetic acid is placed on the paper, which is covered with a bell jar to exclude laboratory fumes; if active oxygen be present a blue ring forms about the acetic acid in the course of one to five hours. Or 5 c.c. of molten fat are shaken with a solution of 5 c.c. of glacial acetic acid and 1 gram of potassium iodide in 50 c.c. of water. In the course of an hour, the active oxygen—if present—will liberate iodine and thus cause the solution to assume a yellow color. The addition of a few drops of starch paste before shaking increases the delicacy of the test, for the blue color of starch iodide is easier to recognize than the yellow color of an aqueous iodine solution. The fat should be melted for these tests at as low a temperature as possible, since heat tends to destroy the peroxides which respond to these reagents. In both modifications of Walker's test, a blank experiment should always be made as a control upon the reagents.

The writer has detected the presence of active oxygen in samples of extracted chicken fat which had been exposed to the action of the air for several months.

DETERMINATION OF THE ACID VALUE OF CRUDE FAT.[38]

In this laboratory the abdominal or gizzard fat of chickens has generally been studied, although the subcutaneous fat has at times been used. The crude fat is passed through a meat chopper several times. Ten grams of the sample are weighed out in a tared Erlenmeyer flask of 250 c.c. capacity; 50 c.c. of alcohol, previously neutralized, are added; and the flask is heated on an electric stove until the alcohol boils briskly. The free fatty acids dissolve in the hot alcohol and are titrated at once with N/10 sodium hydroxide, shaking vigorously. Phenolphthalein is used as an indicator; the end point is shown by a faint pink color, persisting for fifteen seconds.

DETECTION OF LIPASE.[39]

A known quantity of crude fat is ground in a mortar with sand, which has been ignited and permitted to cool to the temperature of the room, then is extracted with ten times its weight of distilled water. The extract is poured through a strainer of wire gauze, then filtered through absorbent cotton. Fifty c.c. of the extract thus prepared are mixed with 1 c.c. of an ester, 1 c.c. of toluol and 0.2 c.c. of a 1 per cent. solution of phenolphthalein in alcohol. The esters more commonly used are ethyl butyrate and amyl salicylate, although many other esters have also been utilized for this purpose. The mixture is made neutral by means of N/10 sodium hydroxide solution. At the same time a blank is prepared by boiling 50 c.c. of the extract, permitting to cool to the temperature of the room, then adding the reagents and neutralizing. Boiling the blank destroys both organized ferments (bacteria, moulds and yeasts) and unorganized ferments (enzymes). In the determination proper, the toluol inhibits the action of organized ferments, but permits the enzymes to react. Both determination and blank are placed in an incubator at 40° C., the optimum temperature for lipase.[40] After the lapse of one or more days, they are again titrated; if the determination proper contain more free acid than the blank, that acid has been liberated from the ester by the lipase, and therefore proves the presence of that enzyme in the crude fat. If necessary, more toluol may be added during the lipolysis to replace that lost by evaporation.

THE ANALYSIS OF MILK.

The methods for the determination in milk of such constituents as total solids, fat, ash and lactose are described in detail in the methods of analysis of the Association of Official Agricultural Chemists[41] and in the various text-books, therefore only certain phases of milk analysis will be discussed in this paper, including the determination of the various nitrogenous compounds, of the lecithin and of the fat by the Roese-Gottlieb method.

The technic for the quantitative determination of the total nitrogen in milk, and of its distribution as casein, albumin and syntonin, caseose, amino acid and ammoniacal nitrogen has been studied in detail in this laboratory.[42] The determination of the

total nitrogen is made upon 5 grams of the milk by the Kjeldahl method as directed by Van Slyke and Hart.[43]

The casein nitrogen is likewise determined by the method of Van Slyke and Hart:[43]

"To about 10 grams add 90 c.c. of water at 104° F. to 108° F. (40° C. to 42° C.) and then 1.5 c.c. of 10 per cent. acetic acid. Agitate and warm at the temperature given above until a flocculent precipitate separates, leaving a clear supernatant liquid. Filter, wash and treat by the Kjeldahl method for estimating nitrogen.

"The use of acetic or any other acid in precipitating casein in milk, whose casein has been digested in any degree, precipitates, in addition to casein, any paranuclein that is present. We have not yet succeeded in devising satisfactory methods for the separation of these compounds."[43]

When milk is kept at low temperatures, the acidity increases and after several weeks is much higher than is required to produce a curd spontaneously at ordinary temperatures, yet the phenomenon of curdling rarely occurs. Such milk must first be made neutral to phenolphthalein by addition of fixed alkaline hydroxide; the casein is then determined in the usual way. The precipitation is best carried out by diluting the milk in a beaker with water of a temperature of 40–42° C., then placing the beaker in a bath of water of that temperature, adding the acetic acid with stirring, and finally filtering as soon as the precipitate is flocculent and the supernatant liquid is clear.

The precipitate of casein is washed with water of a temperature of 40° C., until the washings fail to respond to the biuret test. The albumin and syntonin nitrogen are determined in the combined filtrate and washings from the casein determination by the provisional method of the Association of Official Agricultural Chemists.[41] The solution is neutralized with sodium hydroxide, using phenolphthalein as an indicator, 0.3 c.c. of a 10 per cent. solution of acetic acid are added, the beaker and its contents are placed on an electric stove, the solution is evaporated to a small volume in order to insure complete coagulation of the albumin and syntonin. The precipitate is collected on a filter and washed with boiling water until the washings no longer respond to the biuret test. The filter and precipitate are transferred to a Kjeldahl flask, and the nitrogen is determined.

The quantity of protein, casein and albumin is calculated by

multiplying the total nitrogen of the milk, the casein nitrogen and the albumin nitrogen respectively by the factor 6.38.[41]

The filtrate and washings from the albumin and syntonin are used for the determination of caseose nitrogen. They are combined and evaporated on an electric stove to a volume of 30 c.c., 1 c.c. of 50 per cent. sulphuric acid is added, and the caseoses are precipitated by means of zinc sulphate and determined in exactly the same manner as the albumose nitrogen of flesh was determined (see page 372 for the details of the procedure).

The method for the determination of the amino acid nitrogen is that of Bigelow and Cook.[5] Ten grams of milk are placed in a graduated flask of 100 c.c. capacity, 15 grams of sodium chloride are added, and the flask is placed in an ice box for an hour. Thirty c.c. of an ice-cold 24 per cent. tannin solution are added, the flask is filled to the mark with ice-cold distilled water, and the contents are well mixed. The flask and its contents are kept in the ice-box for 24 hours, then the precipitate is removed by filtration. Both flask and funnel are kept cold during this operation to prevent re-solution of the precipitate. The nitrogen is determined by the Kjeldahl method in 50 c.c. of the filtrate, hence the calculation is made on a sample of 5 grams. A blank determination is also carried out, and due allowance for the nitrogen content of the blank is made in the calculation of the amino acid nitrogen.

The ammoniacal nitrogen in milk is determined by the method of Berg and Sherman[44] with slight modifications. Fifty grams of milk are mixed with 10 grams of sodium chloride, 0.5 gram of sodium carbonate and 50 c.c. of neutral methyl alcohol, in a round-bottomed flask of 2000 c.c. capacity. The flask is provided with a rubber stopper through which pass a distilling head, such as is used in Kjeldahl distillations, and an inlet-tube, which serves to admit air at the end of the distillation. Rubber tubing is attached to the upper end of the inlet-tube and is closed by a screw clamp. A thermometer is suspended from the rubber stopper by means of platinum wire. The bulb of the thermometer and the lower end of the inlet-tube are beneath the level of the liquid in the flask. The distilling head is connected to a series of three Drechsel bottles, which are surrounded by ice-water. Ten c.c. of N/10 sulphuric acid, diluted to 20 c.c. with distilled water, are placed in each of the two Drechsel bottles

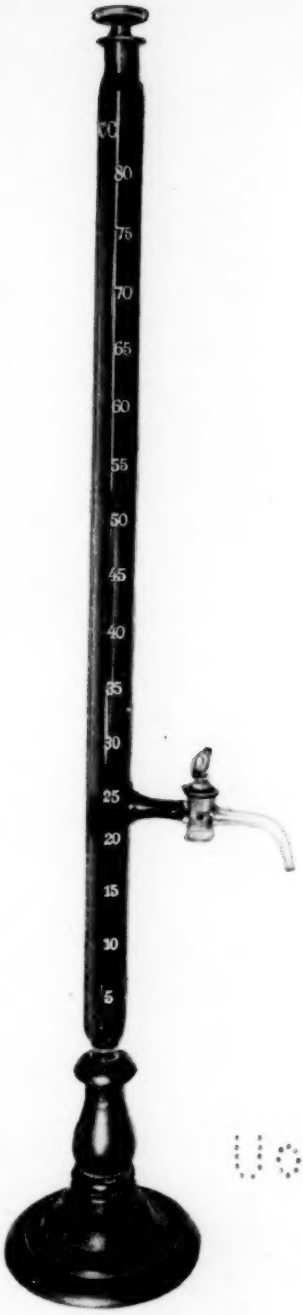
adjacent to the distilling head, while the third bottle serves as a trap and is connected with the vacuum system of the laboratory. All connections by means of rubber tubing are tightly wired. The vacuum pump is started and the flask is placed in a water bath, which has a temperature of 60–65° C. The temperature of the bath is so regulated that the temperature of the liquid within the flask does not rise above 62° C. The sodium carbonate liberates the ammonia from ammonium salts, while the sodium chloride by reducing the hydrolytic dissociation of the carbonate prevents or at least renders "less likely the cleavage of ammonia from organic matter." The methyl alcohol also tends to prevent cleavage by lessening the dissociation of the carbonate and by lowering the boiling point of the liquid. The liberated ammonia distils over and is absorbed by the sulphuric acid in the Drechsel bottles. A low vacuum is used at the start of the distillation and is gradually increased. A period of 15 to 30 minutes is required for the distillation, the end of which is made known by a distinct tendency for the contents of the Drechsel bottles to "suck back." The vacuum cock is then closed, the screw clamp on the inlet-tube is opened at the same time, and air is admitted in such a manner that the distillate is not forced into either the distilling flask or the trap bottle, but remains in its containers. When atmospheric pressure has been restored throughout the apparatus, the distillate is poured into a beaker, the three Drechsel bottles and their connecting tubes are washed with distilled water and the washings are added to the beaker; the solution is diluted to 250 c.c., and the excess of acid is determined by titration with N/10 sodium hydroxide, using cochineal as an indicator. A blank experiment is made upon the reagents, and due allowance is made for the ammoniacal nitrogen content of the blank in calculating the free ammoniacal nitrogen of the milk.

Berg and Sherman state that fresh milk yields the same per cent. of ammoniacal nitrogen, whether sodium chloride be added to or omitted from the contents of the distillation flask. However, after milk has become stale, a higher per cent. of ammoniacal nitrogen is obtained by distilling milk in vacuo at the above temperature with methyl alcohol and sodium carbonate than is obtained by distilling under the same conditions of temperature and vacuum with these reagents plus sodium chloride. The term

free ammoniacal nitrogen is applied to the ammoniacal nitrogen liberated on distillation in the presence of sodium chloride, while the term cleavage ammoniacal nitrogen is applied to the per cent. of nitrogen which remains after the per cent. of free ammoniacal nitrogen is subtracted from the per cent. of total ammoniacal nitrogen obtained by distillation without the use of sodium chloride. If the analytic results be expressed as percentages of ammonia, these terms become free ammonia and cleavage ammonia respectively. Fresh milk contains only free ammoniacal nitrogen, while stale milk contains not only free ammoniacal nitrogen but also certain nitrogenous organic compounds from which cleavage ammoniacal nitrogen is split off during the distillation in the absence of sodium chloride.

The method of Nerking and Haensel [45] in a slightly modified form serves for the determination of the lecithin content of milk and cream. One hundred grams of milk or 25 grams of cream are added to 200 c.c. of alcohol; the mixture is stirred well; after the precipitate has settled, it is removed by filtration. The filter and precipitate are placed in the thimble of a Soxhlet apparatus and extracted for at least 30 hours with chloroform. The alcoholic filtrate is evaporated in vacuo on a water bath at a temperature of 50° to 60° C.; the residue is exhausted by extraction with chloroform, and the extract is added to that obtained from the precipitate. The chloroform solution is transferred either to a nickel crucible or to a Kjeldahl flask and is evaporated to dryness on the water bath; the residue in the crucible is burned with sodium peroxide, while the residue in the flask is digested with sulphuric acid. The details of both methods of procedure are given in the chapter on the determination of phosphorus in fats. The phosphoric acid thus obtained is finally weighed as magnesium pyrophosphate, and the per cent. of phosphoric oxide present as lecithin is calculated; or the per cent. of lecithin itself may be calculated.

The Röhrig tube [46] used in determining fat in milk by the Gottlieb-Röse method is shown in the figure. Ten grams of milk are placed in the tube, and shaken with 1 c.c. of concentrated ammonia water, 10 c.c. of 92 per cent. alcohol are added, the contents of the tube are again shaken, then let stand for a few minutes. Thirty c.c. of ethyl ether are added and the contents



Röhrig tube.

of the tube are mixed by shaking thoroughly for one minute, then 30 c.c. of redistilled petroleum ether of boiling point 40–60° C. are added and the tube is again shaken thoroughly. The liquid is then permitted to separate into two layers. The supernatant liquid, which is a mixture of the two ethers containing the butter fat in solution, is drawn off as completely as possible and permitted to run through a small filter paper into a small tared Erlenmeyer flask; the filter is washed with a mixture of equal volumes of the two ethers. The residual liquid in the tube is extracted as before by adding 30 c.c. of ethyl ether, shaking, adding 30 c.c. of the redistilled petroleum ether, shaking and permitting to separate into two layers. The total volume of the upper layer is noted, and it is drawn off as completely as possible into a second tared flask, filtering as before; the volume thus drawn off is also noted. The two flasks are heated cautiously on the water bath until the solvent has been driven off, then are heated in the water oven at 100° C. until a gain in weight occurs; after each period of heating for 30 minutes the flasks are placed in a desiccator, permitted to cool, and weighed.

It is evident that the mixture of the two ethers which remains in the tube at the end of the second extraction contains butter fat, and that the weight of this fat must be considered in calculating the per cent. of fat in the milk. Hence the weight of fat in the tared flask used in the second extraction is multiplied by the total volume of the second extract, and the product is divided by the volume of that extract which was drawn off; the result is the total weight of fat in the second extract. The total weight of fat in the milk is the sum of the weight thus calculated and the weight of the fat obtained in the first extraction. The per cent. of fat is readily calculated by multiplying the total weight of the fat by 100, and dividing by the weight of milk taken as a sample. This method may be applied to cow's milk and breast milk, and, in modified form,[47] to condensed and evaporated milk, ice cream, milk powder and cheese.

It may be mentioned that, after milk has been clarified in the usual way by means of cupric sulphate and sodium hydroxide,[48] the lactose may be determined by the method of Munson and Walker.[49]

THE ANALYSIS OF EGGS.

The method of separation of the white and yolk of raw eggs for chemical examination has been described in the chapter entitled "Studies of Eggs," in Part II. The methods for the general analysis are quite similar to the methods used in flesh analysis, which have been described in full in the preceding pages. However, only five grams of yolk are taken as a sample for the determination of total solids, moisture, and fat (ether extract); if a larger sample be taken, the thimble of the Knorr extractor is too small to hold the total solids plus the lead dish during the extraction with ethyl ether in the determination of the ether extract. The white is well mixed by passing it several times through a Buchner funnel. The methods for the separation of the various forms of nitrogen in the white are likewise similar to those used in flesh analysis; for the details of the procedure, the original paper of Pennington[14] should be consulted. The mode of extracting the fat from the yolk is given in detail on page 379; the methods of determining the fat constants have also been given in the preceding pages.

The writer desires to acknowledge his indebtedness to Dr. M. E. Pennington and to Dr. E. Q. St. John for assistance and valuable suggestions in the preparation of this paper.

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NOTE.—Part I, "The Function and Equipment of the Laboratory and a Résumé of the Researches Carried Out Therein," appeared in the JOURNAL OF THE FRANKLIN INSTITUTE, June, 1911, CLXXI, 585–598. Part II, "The Scientific Study of the Handling of Perishable Foodstuffs," appeared in the JOURNAL OF THE FRANKLIN INSTITUTE, August, 1911, CLXXII, 173–193.

The Ovifaker Iron; a Natural Carbon Steel. C. BENEDICKS. (*Metallurgie,* viii, 65.)—On examining the specimens of the natural mass of iron discovered at Ovifaker by Nordenskiöld under the microscope, the results show that the mass is a natural steel containing high sulphur. The structure differs from that of meteoric iron, and shows the presence of finely divided pearlite, indicating very rapid cooling below 700° C. A new constituent was observed, which the author terms "oxide-pearlite," in which the cementite lamellæ appear to penetrate into the oxide; this oxide-pearlite was probably formed by a secondary oxidation of the ferrite lamellæ in pearlite. This confirms the view that the mass has been produced by the reduction of the iron compounds in molten basalt by a highly carbonaceous material.

Effects of Ultra-violet Radiations. A. GUNTZ and J. MINGUIN. (*Comptes Rendus,* clii, 372.)—The effects of radiations from a silica Westinghouse mercury vapor lamp, 3.5 amps., at 220 volts, are thus stated. The surface of crystals of benzylidene camphor is corroded, but the melting point and density remain constant. Sugar candy crystals are also corroded, the candy turning yellow, and a certain amount of glucose is produced. Glucose and lævulose are formed by the action of the rays on cane sugar in solution. Anthracene, in benzene solution, polymerises to *p*-anthracene; while phosphorus under water quickly becomes red (amorphous); crystalline sulphur is reduced to powder, and solutions of sulphur in carbon disulphide or benzene deposit an insoluble modification of sulphur.

FRANKLIN INSTITUTE

(Proceedings of the Stated Meeting held Wednesday, September 20, 1911.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, September 20, 1911.

PRESIDENT WALTON CLARK *in the Chair.*

Additions to membership since last report, 4.

The following amendment to the By-laws relating to the election of the Trustees, to be voted on at the next stated meeting, was presented:

Section 2 of Article 1 of the By-laws to be amended to read as follows:

SEC. 2. *Said Board of Trustees shall be composed of seven (7) members, originally elected by the Board of Managers on its own nomination.*

Vacancies, as they occur, shall be filled by election by the Board of Managers from nominations made by the remaining Trustees to a stated meeting of the Board of Managers at least one month prior to the election; the Board of Managers to have the right to reject any nominations not satisfactory to them.

The remaining members of the Board of Trustees, whenever at any time it shall be deemed necessary so to do, shall have power to assign and convey the property held by them, so as to vest the title thereto in themselves and their successors.

Dr. Hugo Lieber, president, H. Lieber & Company, New York, presented a communication on "Modern Uses and Applications of Radium." The speaker reviewed briefly the work of the various investigators in this branch of science and described some of his own researches. He referred to the application of radioactive materials in therapeutics and the action of radium on diseased tissue.

The subject was illustrated by a number of experiments and exhibits.

The thanks of the meeting were extended to Dr. Lieber for his paper. An interesting discussion followed, in which Messrs. Williams, Stratton, Snook, Gartley and Hoadley participated.

Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of proceedings of the Stated Meeting held Wednesday, September 6, 1911.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, September 6, 1911.

DR. GEO. A. HOADLEY *in the Chair.*

Two protests were considered and other business transacted.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

Elections to Membership.

RESIDENT.

MR. CONRAD LAUER, 608 Chestnut St., Philadelphia.

NON-RESIDENT.

MR. FREDERICK D. CHESTER, Chester Springs, Pa.
DR. HUGO LIEBER, 381 Fourth Ave., New York City.
DR. F. J. MACHALSKE, (temporary address) 1618 Wallace St., Philadelphia.

Changes of Address.

MR. WALTER ATLEE, 1406 G. St., N. W., Washington, D. C.
MR. RICHARD GILPIN, 505 Chestnut St., Philadelphia.
MR. J. H. GRANBERY, 145 Milton St., Brooklyn, N. Y.
MR. RUDOLPH HERING, 170 Broadway, New York City.
MR. W. G. MATTHEWS, Matthews, Florida.
MR. HENRY G. MORRIS, Commonwealth Trust Building, Philadelphia.
MR. SAMUEL F. PRICE, JR., 70 W. 46th St., New York City.
MR. JOHN RAE, 5231 Pine St., Philadelphia.
MR. T. EDWARD ROSS, 1209 Morris Bldg., Philadelphia, Pa.
MR. JOHN MORRIS WEISS, Barrett M'f'g Co., Research Dept., Shadyside, N. J.

NECROLOGY.

RESIDENT.

Mr. James C. Brooks, West Chester, Penna.
Mr. James Christie, 100 Rochelle Ave., Wissahickon, Philadelphia.
Mr. Alexander Krumbhaar, Wynnewood, Pa.
Mr. Cyrus Chambers, Jr., Overbrook, Pa.

LIBRARY NOTES.

Purchases.

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WHITTAKER, E. T.—A History of the Theories of Æther and Electricity.
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CURRENT TOPICS

American Mining Congress. The fourteenth annual session of the Congress will be held in Chicago, October 24th to 28th inclusive. The convention promises to be the most successful in the history of the organization, and the following subjects will receive special consideration: The prevention of mining accidents. Workmen's compensation for the victims of mining accidents. The prevention of waste of the natural resources and conservation of the energy which now contribute to coal production. The general problems of the bituminous coal mining industry as intensified by the demand for better protection to miners and the conservation of fuel resources. The Alaskan question. The public land questions of the West as they affect the mining industry.

The Governors of Utah, Wyoming, Idaho and Arizona will lead the discussion of the "Public Land Questions of the West." The Hon. Martin D. Foster, chairman of the House Committee on Mines and Mining, will speak on the relation of Congress to the mining industry. President Bush, of the Missouri Pacific Railroad, will present a statement on the present conditions of the coal industry which will be of special interest to coal operators.

Among the other speakers are President Taft, Secretary Fisher and other officials of the Government.

Action of Caustic Soda on Cotton. J. HÜBNER. (*J. Soc. Dyers and Col.*, xxvii, 126.)—In 1846 Persoz refers to the value of strong caustic soda solution in dyeing manganese bronze on cotton, and to the shrinkage which the fibres undergo. This shows that the action of soda on cotton was known in France before or at the same time that Mercer made his discovery. Persoz says that manganese bronze was first applied to dyeing piece goods by Hartmann de Munster in 1815. The author found a reference to this in "Experimental Researches Concerning the Philosophy of Colours," by Bancroft, published in 1813.

New Methods of Obtaining Hydrogen. R. BLUM. (*Metall. and Chem. Eng.*, ix, 157.)—In the Linde-Frank-Caro process the carbon dioxide of water gas is absorbed by caustic soda; the gas compressed to 60 atmospheres in a three-stage compressor, dried, and cooled by liquid air; the carbon monoxide and nitrogen condense

and the hydrogen escapes. The residue of carbon monoxide is absorbed by soda-lime; and is used as fuel for a boiler or burned in a gas engine. The Carbonium Gesellschaft compress acetylene to two atmospheres and explode it by electric sparks, obtaining lampblack and hydrogen. Last year the company's works blew up. The Internationale Wasserstoff Co. fill retorts with porous iron oxide, reduce the hot oxide with water gas, and then pass steam through the retorts to obtain hydrogen, and recover the iron oxide for fresh use. The Berlin-Anhaltische Maschinenbau A. G. use two gas producers, lined with fire-brick, which are charged with coke; air is blown into the coke by a steam turbine, the blower is stopped and oil sprayed into the producer, yielding lampblack and hydrogen.

Dust Removal in Coal Mines. MAVOR and COULSON. (*Elect. Rev.*, lxviii, p. 833.)—This is a method for removing coal dust from the roadways of mines. Essentially it is an improvement on the vacuum cleaner. The basic principle of the apparatus is to create an artificial dust storm, by means of an air pressure jet, inside a conical nozzle connected to a suction pipe. It consists of four chief parts: (1) A bell-shaped mouthpiece attached by a bayonet joint to a suction hose. Inside the mouth-piece is a nozzle attached to a supply of compressed air, which causes a jet of air to impinge upon the surface to be cleaned, searching out the crevices, and thus raising the dust. (2) A means of obtaining a pressure air jet for disturbing the dust. (3) A means of obtaining air suction to withdraw the dust. (4) A filter or separator to retain the dust collected while allowing the air to escape. Tests with this apparatus are said to have been most successful.

Electrolytic Determination of Zinc in Ores. G. KEMMERER. (*Journ. of Ind. and Eng. Chem.*, ii, 9.)—Zinc can be accurately determined electrolytically when the electrolyte contains 20 to 25 gm. of sodium hydroxide per 100 to 150 c.c., using a current density of 3.1 ampères per square decimetre, a nickel gauze kathode and a rotating anode. The deposits obtained were all of a beautiful bluish-white, and in every case the ferrocyanide test failed to show any zinc in the remaining solution. 0.17 to 0.37 gm. of zinc was deposited in 10 to 20 minutes.

A Method of Calibrating Fine Capillary Tubes. T. R. MERTON. (*Phil. Mag.*, xxi, p. 386.)—The bore of a capillary tube is, as a rule, determined by optical measurement of the bore and by weighing a drop of mercury occupying a known length of the tube. These experiments were made in order to ascertain the accuracy with which a measurement of the electrical resistance of a fine glass capillary tube filled with mercury can be determined. From this a mean value for the radius of the tube is computed. Correction for

the curvature of the stream-lines of current at the ends of the tube must be made. The results prove the simplicity and accuracy of the method.

A Method of Observing Stream-lines in Air. A. LAFAY. (*Comptes Rendus,* clii, 318.)—This is done by using a thin stream of acetylene issuing from a nozzle 2 to 3 mm. in diameter, which when illuminated casts upon a screen a refraction shadow of one bright line between two dark ones; thus the path of the gas is rendered visible. The acetylene should flow from the nozzle at the same velocity as that of the air current in which it is immersed. By this method variations in the speed of the air can be detected by the discontinuity of the shadow. The acetylene will have the same density as the air if it is cooled to about 30° C. below the temperature of the air, or if it is mixed with CO_2 in the proportion of $8C_2H_2$ to $3CO_2$. If the smell of acetylene is too objectionable, substitute ethylene.

Zodiacal Light. BIRKELAND. (*Comptes Rendus,* clii, 345.)—Several observers have noted that the zodiacal light sometimes presents very regular pulsations in intensity and form. The author finds that these pulsations correspond very closely with the periods found for regular magnetic waves in the polar regions; which suggests that the zodiacal light may have an electrical origin. Several experiments are described which were undertaken in the endeavor to confirm this view. From these it is inferred that there may be a ring of luminous matter extending in the plane of the sun's magnetic equator. There are references also to the *Gegenschein* and the formation of luminous clouds.

Definition of Intensity of Electric Current. A. OCCHIALINI. (*N. Cimento,* Ser. vi, 1, p. 65.)—Instead of the usual definitions based on hypothesis, this is an attempt to deduce a definition of intensity of current directly from experiment. By connecting a Wimshurst machine with a Grassi voltameter and a Leyden jar, it can be shown that the quantity of an electrolyte decomposed in a voltameter is independent of the time taken by the current to pass through it, of the dimensions and form of the voltameter, and also of the physical condition and concentration of the solution; depending only on, and being proportional to, the quantity of electricity. Hence the intensity of the current can be defined in terms of the quantity of the electrolyte decomposed.

Bright Color of Bronze and Composition Castings. ANON. (*Brass World,* vii, 8, 268.)—On the best grade of steam metal goods there is frequently found a bright, clean color, which some believe

is obtained by an acid dip; but this is not the case. This color is due to plunging the casting at a low red heat into cold, clean water. This good color is only obtained under the following conditions: The bronze or composition must be of good quality, and must not contain too much lead, iron, antimony or other impurities. Copper ingot makers succeed in producing the beautiful rose-red color on the best grade of Lake copper ingots by the use of cold, clean water.

Cold Storage Equipment. ANON. (*Times Eng. Suppl.*, June 28, 1911.)—The ammonia system requires less power than the carbon dioxide system and is better adapted for cooling by direct expansion in tubes in the refrigerating chamber. In small plants the compressors are often driven by electric motors, and in large plants by suction gas plants. Atmosphere condensers, *i.e.*, tubes cooled by exposure to air and a water spray, require 50 to 70 per cent. less water than submerged condensers cooled by water alone. The power required for the compressors is about 1½ H. P. per ton of "refrigerating capacity" per day, equivalent to about 3 H. P. per ton of actual ice-making capacity. To cool the refrigerating chamber by air currents, previously cooled, electrically driven fans are used. A 5 or 6 H. P. motor is sufficient to drive the fans for an air-cooler supplying 80,000 to 100,000 cubic feet of storage space.

Amount of Radium in Some Uranium Ores. W. MARCKWALD and A. S. RUSSELL. (*Chem. News*, ciii, 277.)—The radium in a number of uranium ores was determined by dissolving in strong sulphuric acid, in which radium sulphate is soluble, and measuring the emanation evolved by means of its ionizing power. If the ratio of radium to uranium in Joachimsthal pitchblende is taken as 100, then the ratio in thorianite is 98.1, and in African pitchblende 101.5, but in autunite it varies from 20.7 to 68.0. A determination of ionium in autunite showed that the ratio of ionium to uranium is much more uniform than that of radium to uranium, and is also relatively higher. Since ionium's mean duration of life is not less than 30,000 years, this indicates that autunite must be at least 100,000 years old, and the relatively low numbers of the radium ratio cannot be explained by assigning to it a recent origin, as Soddy suggested. The facts are accounted for by supposing that on account of its spongy structure, as compared with the very dense pitchblende and thorianite, radium and lead have been partially extracted from the mineral by water, the occlusion of helium also being very slight. The results obtained with rutherfordite support this view.

Iron in Nickel. ANON. (*Brass World*, vii, 8, 294.)—The presence of iron in nickel makes it whiter. All nickel anodes and nickel deposits contain iron. This deposit, containing iron, although whiter than one free from iron, is more readily tarnished.

The Action of Salt Solutions and Sea-water on Iron. J. A. N. FRIEND and J. H. BROWN. (*Chem. Soc. Proc.*, xxvii, 156.)—Thin plates of pure iron were exposed to the corrosive action of various concentrations of common salt and of sea-water at different temperatures. Below 13° C. (55.4° F.) dilute solutions exert a more corrosive action than distilled water at the same temperature; above 13° C. they are less corrosive. At 13° C. the corrosive action is practically the same for dilute solutions of salt, for ordinary sea-water, and for distilled water. Therefore this temperature is named the "inversion temperature."

The Rôle of Slags in Smelting Processes. C. DICHMANN. (*Stahl und Eisen*, xxxi, 749.)—This considers the solubility of silica, bases, and silicates in each other. The slags of heating furnaces are said to be simple solutions of iron oxide in silicates, and therefore furnaces should be repaired with silica and not with bases. Each kind of furnace used in the steel industry is discussed, and it is shown that iron phosphide is removed by ferrous silicate, being oxidized to phosphate; hence to insure its removal the slag must contain plenty of oxygen.

Detecting Adulteration of Oils. ALEX. E. OUTERBRIDGE, JR. (*Iron Age*, lxxxviii, 2, 91.)—This is a valuable article for all users of lubricating oils, and is well worth their close attention. The gist of it may be stated as follows: De-bloomed mineral oils are free from bloom (fluorescence) in bright sunlight, or ordinary diffused daylight, or the light from an ordinary electric arc, but *they all become highly fluorescent* when exposed to the *ordinary enclosed arc;* which happens to give out rays of the exact wave length needed to enormously increase the fluorescence. The light should be so inclosed that the arc burns in a partial vacuum or at least the air is rarefied, and after burning a minute gives a faint rosy light in addition to the powerful white light. If a vessel containing any mineral oil, crude or refined, or any resin oil, be placed in the path of these rays, the most intense fluorescence appears, even in daylight; greenish in the case of mineral oil and blue in the case of resin oil; thin films glowing in the same manner. So strong is the fluorescence that 1 c.c. of crude mineral oil has been detected in 999 c.c. of non-fluorescent oil. "It is stated in some text-books that 'oleic acid' which is found in lard oil is fluorescent. On examination I find that pure, white, strained lard oil is entirely free from fluorescence under the ultra-violet ray, but all of the samples of so-called No. 1 or No. 2 lard oil (sold for use in machine shops) examined possess some fluorescence, and this may prove to be a novel means of rapidly determining the proportion of oleic acid in lard oil, though I only suggest it tentatively." To carry out this test systematically, it is desirable to put the standards in narrow, tubular, oil-test bottles, holding about 50 c.c. each; corked, labelled, and placed side by side in small

wooden racks on a shelf in proximity to an inclosed arc light; beginning with a pure oil on the left hand side, then bottles with 0.1 per cent. mineral oil, 1 per cent., 2 per cent., etc., up to 10 per cent. The standard with linseed oil serves to examine cottonseed, corn, China-wood, China-bean oils, or any other non-fluorescent vegetable oil. The special standard of lard oil is necessary to test adulterated lard oils.

Materials for Balloon Envelopes and for Producing Gas-tightness. H. HOERNES. (*Gummi-Zeit.*, XXV, 1281.)—The materials used for balloon envelopes are: (1) *Pongee Silk.* Its advantages are its great tensile strength combined with lightness; its disadvantages are its high cost, its tendency to brittleness, and its electrical properties. (2) *Cottons,* such as *Percale* or *Calico.* Their advantages over silk are greater stability as regards atmospheric influences, but they are less strong and much heavier. Generally employed as a double layer of the fabric, with the threads either parallel or at an angle of 45° to one another, joined by an intermediate layer of rubber. (3) *Fine Linen.* Almost as costly as silk, but not as light, and therefore not desirable. (4) *Gold-beater's Skin* is very expensive, difficult to repair, and sensitive to atmospheric influences. Advantageous on account of low porosity and its high tensile strength per unit weight. (5) *Aluminum* is used in strips of sheet about 0.2 mm. thick, riveted or welded together. The materials for gas-tightness are: (1) *Linseed Oil Varnish.* Advantageous on account of low cost and ease of application and great efficiency. Objections are the need of constant attention during storage, risk of spontaneous inflammation if the air supply is insufficient, the slowness of the repairing process and tackiness at an elevated temperature. (2) *Rubber.* Used as a layer of vulcanized rubber between the layers of fabric. Repairs effected easily and rapidly, the fabric is always supple and there is no tackiness at high temperatures. On the other hand, it is high priced, susceptible to electric discharges. very heavy, and easily affected by the violet and ultra-violet rays. Other gas-tight materials are *Ballonin,* a solution of gutta-percha in benzol; *Konjaku,* a Japanese vegetable product, put on the market as a white powder, soluble in warm water; *Bi-chromated Gelatin;* and *Pegamoid.*

Solder for Aluminum. N. J. A. BOURGADE. (*French Patent,* 425, 912, 1910.)—The solder is composed of an alloy of 1 part tin and 2 parts zinc, to which 5 per cent. of its weight of cadmium is added. These proportions are variable. The solder can be used without a cleansing agent or solvent for oxide.

The Influence of Surface on the Rusting of Iron. K. ARNDT. (*Metallurgie,* viii, 353.)—The electrolytic theory of the rusting of iron is discussed in relation to the varieties of iron, such as cast iron

and machined products. Graphitic grains form centres from which rusting starts. Fractures rust more readily than the outer surface, and it is suggested that a coating of silicates in the case of cast iron, and films of scale in rolled material, act as a protecting layer. The rough surface of a fracture distinctly accelerates rusting. Smooth surfaces are more resistant than rough ones.

Hardening Copper. (*U. S. Pat. No. 984,137.*)—R. A. Hamilton and J. Henry harden copper by treating it with a mixture of aluminum and iron pyrites. The aluminum is heated to a high temperature in a crucible and enough pyrites added to it to form a brittle compound, which is poured into moulds. From 1 to 3 oz. of this mixture, with charcoal and borax, are added to each pound of copper already melted.

Electric Smelting of Iron Ore at Trollhätten, Sweden. ANON. (*Board of Trade J.*, June 29, 1911.)—The report of the Swedish "Jernkontoret," or Iron and Steel Institute, for 1910, gives the results of the experiments made at Trollhätten in the smelting of iron ore by electricity, provided at low cost from the Government works. The plant cost £17,800. Operations began Nov. 15, 1910. The results show that the question of smelting iron ore by electricity is solved even from the economical point of view, if electricity is provided at low rates. Better results are expected if the gas can be more effectively circulated, which seems feasible with better arrangements. The experiment has paid expenses. It is considered that the smelting works cannot be a commercial success if the cost of electricity should exceed the present rate of £2 4s. 5d. ($11.00) per kilowatt per annum. In a five months' run the consumption of charcoal was 413 kilos per ton of iron, and of electricity 1 kilowatt per annum for 4 tons. The product was practically free from slag and oxide. Satisfactory results were also obtained at the works at Fagersta, Eskilstuna, Hagfors, and Munkfors.

Mineral Resources and Industry of Bolivia. ANON. (*Board of Trade J.*, July 6, 1911.)—Indications of gold are found all along the eastern slope of the Cordillera Real, and in the beds of the rivers flowing east from this range. The annual production of gold in Bolivia may be reckoned as 17,460 ounces of bullion, value at £72,000. The richest silver region lies in the west. In the north, south and east the silver lodes are found near the summits of the Andean range, running east and west. There is little silver in the north. The production of silver fell from £1,474,495 in 1895 to £54,472 in 1909. This diminished output is attributed to the fall in the price of the metal, and the increase in the value of tin, which is abundantly found close to the silver-bearing areas and in an easily worked condition. The silver mine owners have diverted their work and capital to tin production. Copper is found widely distributed over the

highlands of Bolivia, and extending into Peru. The province of Pacajes contains the richest copper region, southwest of Lake Titicaca, known as Corocoro. The production has risen from 1518 metric tons in 1885 to 3084 metric tons in 1909. Tin is found principally in the higher peaks of the Cordillera Real, overlooking the basin of the Amazon. The ore averages 5 to 10 per cent. High grade stream tin is also found. In most operations the ore is merely crushed and washed, and concentrates of 55 to 65 per cent. tin are exported. Bolivia is the second tin-producing country in the world, only surpassed by the Straits Settlements. The principal beds of tungsten in Bolivia are in the province of Calugo, department of La Paz. The picked ore contains tungstic acid 75 to 76 per cent., ferric oxide 10 to 20 per cent., manganese oxide 4 to 15 per cent. Pools of petroleum oil and pitch are found in Eastern Bolivia extending over 300 miles, in a narrow belt.

Canadian Asbestos. ANON. (*Chamber of Comm. J.*, July, 1911.)—Canada produces 82 per cent. of the world's supply of asbestos. The capitalization of the asbestos quarries and factories of Canada amounts to $24,290,000. In 1880 only 380 tons were produced, in 1909 the output was 63,300 tons, and 2000 men were employed. In the Black Lake quarries, province of Quebec, there are 45,000,000 tons of asbestos rock in sight. The Russians are the only real rivals as regards extent of asbestos resources, but are handicapped by the cost of transportation, $35 to $40 per ton, from the mines to London. The asbestos slate or shingle industry is being developed in Canada, and it is predicted that in a short time 75 per cent. of all the asbestos produced in Canada will be used for this purpose. This asbestos slate business is only five years old, yet the demand has increased enormously, and large factories are established to supply this new roofing material.

Simultaneous Manufacture of Silicon and Pure Alumina. F. LAUR. (*French Patent*, 425, 277, March 31, 1910.)—To produce pure alumina for the manufacture of aluminum, it has hitherto been necessary to use bauxite containing a very little silica. To produce pure alumina from very siliceous bauxites, or from natural silicates, the white bauxite or kaolin may be crushed and mixed with coke, using only just enough carbon to reduce the silica (0.4 part carbon for 1 part silica). The mixture is smelted in the electric furnace, when the silicon is separated and a slag of nearly pure alumina obtained. To free the alumina from the last traces of silica, a little powdered aluminum carbide (1 per cent. for each 1 per cent. of silica) is then added whilst the liquid is stirred. This liberates the last of the silicon and separates it from the alumina, which can be removed and pulverized.

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* Deceased